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PREPARATION AND EVALUATION OF NEW SORBENTS FOR ENVIRONMENTAL MONITORING

VOLUME I

by

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Sixty-one different polyimide sorbents were prepared for evaluation as sorbents for the collection of vapor-phase organics in ambient air. Laboratory tests were applied to evaluate their properties as sorbents and to develop a data base to examine relationships between chemical structure and physical properties.

A tiered level-of-effort testing was applied. The Level I procedure sorted the polymers according to specified desired properties; Level II testing provided information for selecting the most promising polymers for trapping of vapor-phase organics and generated the chemical data base relating chemical and physical sorbent properties, and Level III experiments provided a confirmation of the physiochemical properties of the sorbent. Thermodynamic properties and correlations between chemical structure and physical properties were made for four of the more promising polyimide sorbents and compared to Tenax GC, the reference sorbent.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Pesticides and Toxic Substances, and the Office of Solid Waste and Emergency Response.

The concentration of toxic organic vapors in ambient air may be as low as a few nanograms per cubic meter and still have biological consequences. Consequently the determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. Since analytical techniques are not sensitive enough for *in situ* detection, pre-concentration of the sample is necessary. Tenax GC, the most widely used sorbent for the collection of volatile toxic organics from air has been shown to lack selectivity for certain classes of lower molecular weight organics and has been shown to produce artifacts.

The present investigation was undertaken to synthesize new solid sorbents that would either replace or complement Tenax GC for the collection of toxic organic vapors from ambient air. Limited laboratory evaluations of performance parameters and break-through volumes indicated that several of the newly synthesized sorbents are potential candidates to replace or complement Tenax GC.

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Director
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ABSTRACT

Sixty-one different polyimide sorbents were prepared for evaluation as sorbents for the collection of vapor-phase organics in ambient air. Laboratory tests were applied to evaluate their properties as sorbents and to develop a data base to examine relationships between chemical structure and physical properties.

A tiered level-of-effort testing was applied. The Level I procedure sorted the polymers according to specified desired properties; Level II testing provided information for selecting the most promising polymers for trapping of vapor-phase organics and generated the chemical data base relating chemical and physical sorbent properties; and Level III experiments provided a confirmation of the physiochemical properties of the sorbent. Thermodynamic properties and correlations between chemical structure and physical properties were made for four of the more promising polyimide sorbents and compared to Tenax GC®, the reference sorbent.

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SECTION 1

INTRODUCTION

The concentration of hazardous vapors in ambient air may be as low as a few nanograms per cubic meter and still have biological consequences. Because analytical techniques are not sensitive enough for in situ detection, preconcentration of the sample is necessary.

There are several methods for collecting vapor-phase organics from the atmosphere. These include: (a) cryogenic systems, (b) solvent impingers, (c) evacuated canisters, (d) polymeric bags, and (e) sorbent cartridges. The mechanism of trapping vapor-phase organics by each of these methods differs. For cryogenic traps, the principal mechanism is condensation using very low temperatures and, therefore, selectivity may be based on the temperature employed. With solvent impingers, the vapor-phase organics are dissolved in a liquid and the selectivity may be derived from the solvent properties of the particular liquid included in the impinger. To a limited extent, selectivity may also be achieved with temperature. The use of evacuated canisters and polymeric bags is not preconcentration; these are simply containers that are first evacuated and then filled with the ambient air. Sampling with sorbent cartridges involves the adsorption of organic vapor on a solid surface and its selectivity is based upon its chemical structure and, to a marked extent, the temperature at which the trapping occurs.

A number of problems exist with the use of any one of these particular methods for collecting and/or concentrating organic vapors from ambient air. Sampling of ambient air involves the concentration of organics occurring at very low levels (ppb-ppt) in the presence of high levels of water vapor. Also, reactive inorganic species such as ozone, OH radicals, NO_x, and SO_2 are present which perturb the qualitative and quantitative organic composition during the sampling process.

Several problems are associated with cryogenic traps, one of which is the condensation of considerable quantities of water. Artifact products may occur from solution chemistry. For example, the presence of NO_x and SO_x in the ambient air results in the production of an acid solution (nitrous/ nitric acid and sulfuric acid) which can create artifactual products during the recovery of the sample from the trap. Furthermore, the sample is diluted into an aqueous phase which increases the difficulty of subsequent analysis since a concentration step still must be employed or a method for water removal must be instituted. Techniques have been applied for removing water, such as the use of Napthion® tubing which is highly permeable to water while retaining organics. However, it is not completely selective for all organics since very polar materials may also penetrate and pass through this polymeric membrane.

Similar problems are observed with the use of solvent impingers, i.e., artifacts from solution chemistry and the trapping of low levels of organics in a dilute medium, in which low detection levels cannot be achieved.

Evacuated canisters and polymeric bags are not concentrating methods, but simply contain sample which is subsequently concentrated in a cryogenic inlet- manifold for injection into an analytical system such as gas chromatograph.

Preconcentration has been accomplished most successfully using porous polymeric sorbents. Sampling techniques for hazardous vapors utilizing porous polymer beads in cartridge form have been extensively studied by the Research Triangle Institute under a number of EPA contracts (e.g., Rpt. Nos. EPA-600/7-78-062, EPA-600/2-79-081, EPA-600/2-79-027, and NTIS No. RTI/1870/00). During the course of this work many sorbent materials had been evaluated. Sorbents of the polystyrene type - Chromosorb 101, 102, 104 - have been shown to adsorb hydrocarbons, alcohols, acids, esters, aldehydes, ketones, ethers, and glycols. Tenax GC®, a porous polymer of 2,6-diphenyl-para-phenylene oxide, has been shown to adsorb representative members of classes of compounds suspected of being carcinogenic or mutagenic. These commercial sorbents do exhibit selectivity. However, even a higher degree of specificity is desirable. A need for greater selectivity had become apparent through the use of these materials. In general, less than 20% of the chromatographic peaks in ambient air samples are due to halogenated or oxygenated compounds. The balance is largely aromatic and aliphatic hydrocarbons. The presence of such a multitude of aromatic and aliphatic hydrocarbons precludes complete resolution of the mixture and thus obscures trace components and requires the expenditure of an excessive amount of effort for their identification. For this reason, greater selectivity in sorbents is sought for collection of ambient air pollutants. Furthermore, the more volatile vapor-phase organics such as methyl chloride, methyl bromide, vinyl chloride and vinyl bromide, as well as acrylonitrile, methylene chloride and chloroform, are not adequately retained by the sorbent Tenax GC®. Thus, a more retentive sorbent would be desirable. However, the sorbent must have good thermal properties, i.e., a minimal background contribution (to avoid sample contamination), a low retentive volume for water vapor, and resistance to the reactive inorganic gases ozone, NO_x, and SO_2 which occur in ambient air. The most desirable sorbent would yield minimal artifacts during the collection of reactive organic compounds.

The purpose of this research program was to examine the problems that have been identified with the use of solid sorbents for air monitoring for organic compounds of interest to the Environmental Protection Agency under previous research programs. Of particular interest were the organic types which include compounds of four or fewer carbons, polar neutral species, organic acids, organic bases, halocarbons and halohydrocarbons, and compounds boiling above and below those which are amenable to monitoring using Tenax GC®. Another objective of this research program was to develop and report a stepwise testing procedure structured at different levels of effort to provide a cost effective route to screening solid sorbents and testing them rigorously. Such a test procedure has been prepared as a separate document. The purpose of the test procedure is to provide definitive information on empirical parameters of interest which could be used to derive the rationale for a systematic study. The test procedure has been designed to obtain information relating chemical structure to physical properties of sorbents. Development of a theory for predicting sorbent properties from polymer structures was thus a specific aim of this research program.

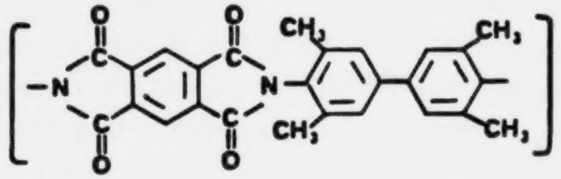
As a part of this testing procedure, consideration was made of tests to be conducted on synthetic (laboratory) and on real field samples, including artifact formation, shelf life of blanks, storage life of exposed samples, precision, and accuracy, i.e., parameters relating to quality assurance.

SECTION 2

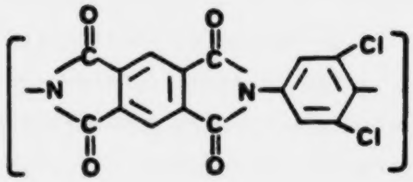
CONCLUSIONS

Forty-two different aromatic diamines were selected from a list of 47 commercially available ones to be used in combination with pyromellitic dianhydride (PMDA) for the preparation of polyimide sorbents. In addition to polyimides based on PMDA, 19 different polyimides were prepared utilizing benzophenone tetracarboxylic dianhydride.

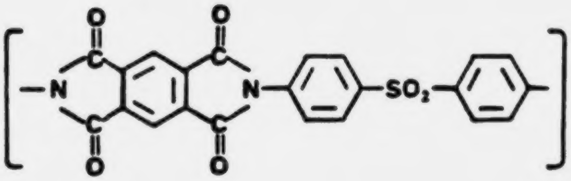
Of the polyimides that were synthesized, four were selected with the most desirable characteristics from the chemical and physical data derived from Level I and Level II testing. These polyimides have the following structures:



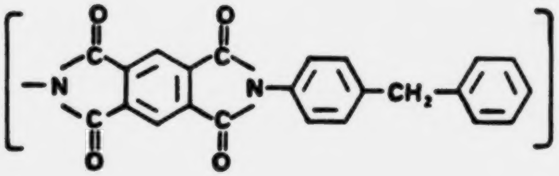
PI-109



PI-115



PI-119



PI-149

The four polyimide sorbents (PI-109, PI-115, PI-119 and PI-149) were then submitted to Level III testing for confirmation as candidate sorbents for possible use in ambient air sampling.

The breakthrough volumes derived from frontal and elution chromatography experiments were compared for a series of test compounds and polyimides. The overall agreement was fair for data derived from each of the methods, to underscore the legitimacy of both methods for generating breakthrough volume data. The specific retention volumes for all test substances were one to two orders of magnitude greater for polyimide sorbents than for Tenax GC®. The specific surface areas being comparable, the affinity of polyimide sorbent for specific and nonspecific interaction with solutes was significantly higher.

Thermodynamic parameters for adsorption, such as adsorption coefficients and adsorption enthalpies, were calculated and were found to be appreciably higher than those derived for Tenax GC®. A model was derived, based upon the solubility parameter concept using specific retention volume data, for correlating chemical and physical sorbent properties. The use of multiple correlation of specific retention volumes with expanded solubility parameters allowed the calculation of expanded solubility parameters of the sorbent. In general, a correlation analysis of retention data using solubility parameters has great potential in these types of studies. The prediction of retention volumes using a linear regression model was also tested to determine whether the retention volumes for solutes could be predicted on sorbents synthesized in this program. Calculated and experimental retention volumes gave satisfactory agreement for purposes of predicting which chemical structures, i.e., sorbents, will yield desired retention characteristics for target solutes.

SECTION 3

RECOMMENDATIONS

This research program has derived a model for the prediction of the chemical structure of a polymer that should be prepared to adsorb target atmospheric pollutants. Further work on the synthesis and testing of additional polyimide structures should be performed in order to enlarge the data base for additional correlation studies. Four of the 61 synthesized polyimides (see Section 2) which were selected as the best candidates according to test data derived from Level I, II, and III testing should be further evaluated as sorbents for use in ambient air sampling. Investigations on the preparation of large pure batches of these polyimides should be undertaken.

Also, the selected sorbents should be field tested under a variety of ambient air conditions. A rigorous experimental design should be devised to develop the necessary field-associated information for the newly synthesized polyimide sorbents.

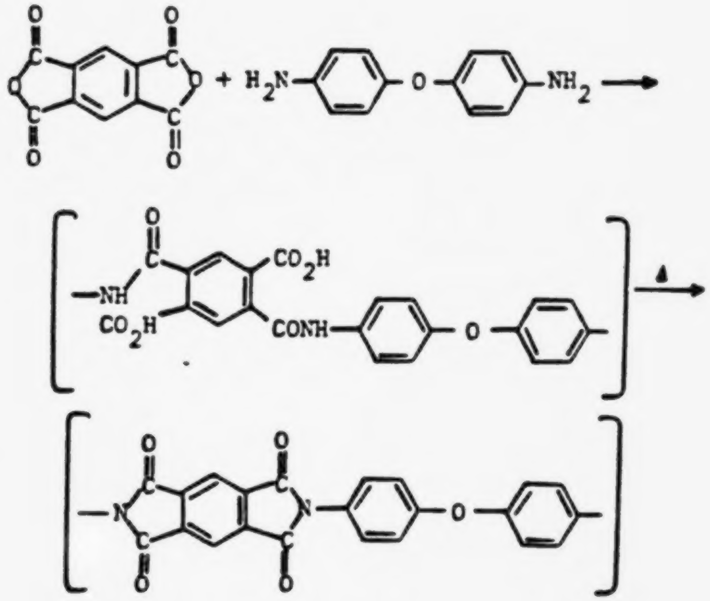
SECTION 4

SYNTHESIS OF POLYMERIC SORBENTS

INTRODUCTION

Aromatic polyimides exhibit outstanding thermal properties, particularly polyimides derived from pyromellitic dianhydride (PMDA), which remain stable up to 500°C if heated under vacuum or in an inert atmosphere. The thermal stability is sharply reduced by the introduction of aliphatic linkages, and weight loss may start at 200-300°C depending on the chemical structure.

Polyimides are prepared in a two-stage process. During the first stage a poly(amide-acid) precursor is formed by reacting an aromatic dianhydride with a stoichiometric amount of an aromatic diamine in an aprotic reaction medium. The reaction is generally performed at ambient or slightly elevated temperatures (up to 70°C) depending on the reactivity of the diamine. Extremely reactive diamines can be reacted even at 0°C or below. The isolated precursor polymer is then cyclodehydrated to the polyimide by either chemical or thermal treatment.



High molecular weight products are obtained under the homogeneous reaction conditions of poly(amide-acid) formation by utilizing, among others, solvents such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, pyridine, or N-methyl-2-pyrrolidone. All of these solvents are rather unfavorable for the preparation of polymeric sorbents because they are strongly bound to the polymer and are subsequently difficult to remove due to their high boiling points. In low boiling solvents, such as tetrahydrofuran (THF), the poly(amide-acids) are generally insoluble and the polymerization proceeds heterogeneously. Because of the insolubility of poly(amide-acids) in THF, polymers obtained in THF possess lower molecular weights than those obtained in solvents sustaining homogeneous reaction conditions. The use of polyimides as sorbents does not require very high molecular weight products but demands extremely pure polymers. For this reason, THF was utilized in all preparations since the sacrifice in molecular weight is more than compensated by improved polymer purity.

Chemical cyclodehydration of poly(amide-acids) can be performed with acetic anhydride-pyridine mixtures at ambient temperatures. Under these conditions the polymers are in contact with high boiling solvents, traces of which are difficult to remove. The preferred cyclodehydration method for sorbent preparation is the thermal process which only involves heating of the poly(amide-acid) to 230°C under vacuum or in an inert gas stream for several hours.

Polyimides of different chemical structures were obtained from a combination of two common aromatic dianhydrides, pyromellitic dianhydride (PMDA) and 2,2',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), with a large number of commercially available aromatic diamines. The diamines utilized for the preparation of polyimide sorbents are presented in Tables 1 thru 6. They are grouped according to the heteroatoms in their structures and are coded as follows:

Diamine Code	Heteroatom	Table
F-I thru F-IV	Fluorine	1
Cl-I thru Cl-VII	Chlorine	2
N-I thru N-VI	Nitrogen	3
S-I thru S-VII	Sulfur	4
O-I thru O-VI	Oxygen	5
C-I thru C-XVII	none	6

Table 1. STRUCTURAL UNITS -R- OF FLUORINATED AROMATIC DIAMINES $H_2N\text{-}R\text{-}NH_2$

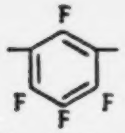
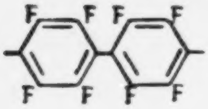
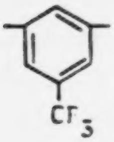
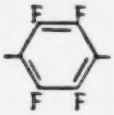
	F-I	Tetrafluoro-*m*-phenylenediamine
	F-II	Octafluorobenzidine
	F-III	3-Trifluoromethyl-*m*-phenylenediamine
	F-IV	Tetrafluoro-*p*-phenylenediamine

Table 2. STRUCTURAL UNITY -R- OF CHLORINATED AROMATIC DIAMINES $H_2N\text{-}R\text{-}NH_2$

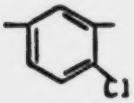
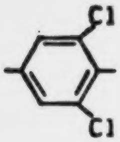
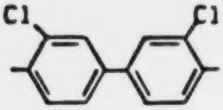
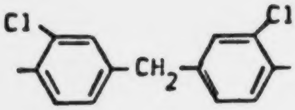
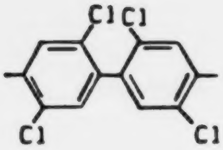
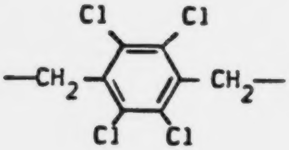
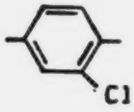
	Cl-I	4-Chloro-*m*-phenylenediamine
	Cl-II	2,6-Dichloro-*p*-phenylenediamine
	Cl-III	4,4'-Diamino-3,3'-dichlorodiphenyl
	Cl-IV	Bis(4-amino-3-chlorophenyl)methane
	Cl-V	2,2',5,5'-Tetrachlorodiphenyldiamine
 Cl Cl CH2 CH2 Cl Cl	Cl-VI	α,α'-Diaminotetrachloro-*p*-xylene
	Cl-VII	2-Chloro-phenylenediamine

Table 3. STRUCTURAL UNITS -R- OF NITROGEN-CONTAINING AROMATIC DIAMINES

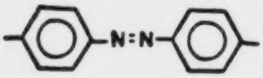
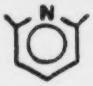
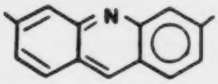
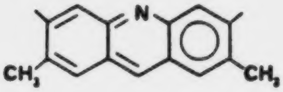
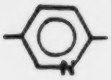
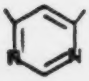
Structure	Code	Diamine
	N-I	4-Azo-dianiline
	N-II	2,6-Diaminopyridine
	N-III	3,6-Diaminoacridine
	N-IV	3,6-Diamino-2,7-dimethylacridine
	N-V	2,5-Diaminopyridine
	N-VI	4,6-Diaminopyrimidine

Table 4. STRUCTURAL UNITS -R- OF AROMATIC DIAMINES CONTAINING SULFUR

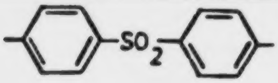
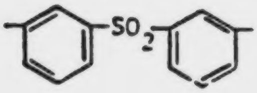
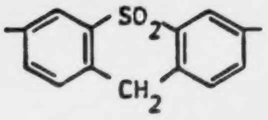
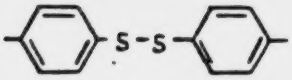
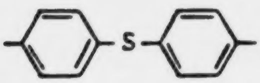
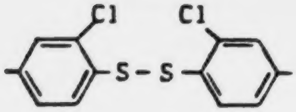
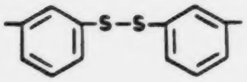
	S-I	Bis(4-aminophenyl)sulfone
	S-II	Bis(3-aminophenyl)sulfone
	S-III	4,4'-Diaminodiphenylmethane-2,2'-sulfone
	S-IV	Bis(4-aminophenyl)disulfide
	S-V	Bis(4-aminophenyl)sulfide
	S-VI	4,4'-Diamino-2,2'-dichlorodiphenyl-disulfide
	S-VII	Bis(2-aminophenyl)disulfide

Table 5. STRUCTURAL UNITS -R- FOR OXYGEN-CONTAINING AROMATIC DIAMINES

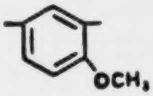
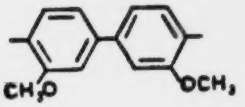
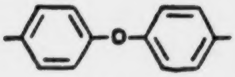
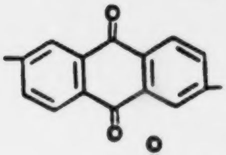
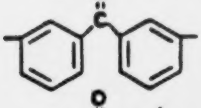
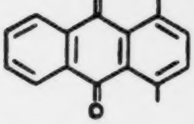
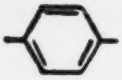
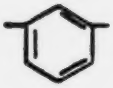
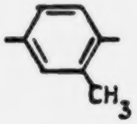
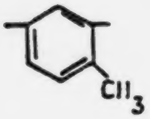
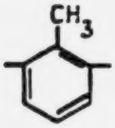
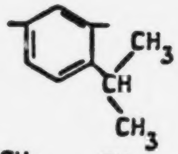
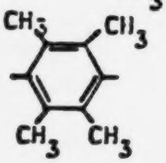
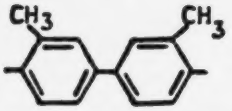
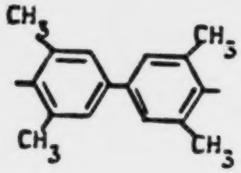
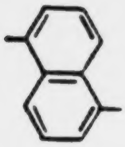
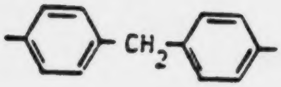
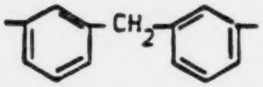
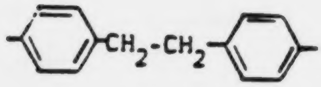
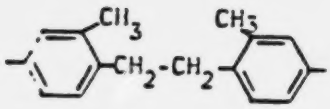
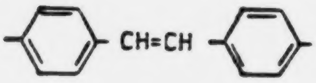
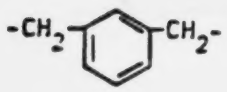
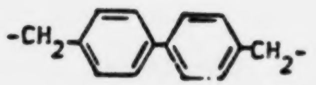
Structure	Code	Diamine
	O-I	2,4-Diaminoanisidine
	O-II	o-Dianisidine
	O-III	Bis(4-aminophenyl)ether
	O-IV	2,6-Diaminoanthraquinone
	O-V	3,3'Diaminobenzophenone
	O-VI	1,4-Diaminoanthraquinone

Table 6. STRUCTURAL UNITS -R- FOR AROMATIC DIAMINES WITHOUT HETEROATOMS

Structure	Code	Diamine
	C-I	p-Phenylenediamine
	C-II	m-Phenylenediamine
	C-III	2,5-Diaminotoluene
	C-IV	2,4-Diaminotoluene
	C-V	2,6-Diaminotoluene
	C-VI	2,4-Diaminocumene
	C-VII	Tetramethyl-p-phenylenediamine
	C-VIII	o-Toluidine

(continued)

Table 6 (cont'd.)

Structure	Code	Diamine
	C-IX	3,3'-5,5'-Tetramethylbenzidine
	C-X	1,5-Diaminonaphthalene
	C-XI	Bis(4-aminophenyl)methane
	C-XII	Bis(3-aminophenyl)methane
	C-XIII	1,2-Bis(4-aminophenyl)ethane
	C-XIV	4,4'-Ethylene-*m*-toluidine
	C-XV	4,4'-Diaminostilbene
	C-XVI	α,α'-Diamino-*m*-xylene
	C-XVII	4,4'-Diaminobibenzyl

Polyimides prepared with PMDA are numbered PI-101 thru PI-173; those prepared with BTDA are numbered PI-201 thru PI-219, with the numbers increasing in consecutive order of preparation. All preparations performed are listed in Table 7 for PMDA and in Table 8 for BTDA.

EXPERIMENTAL METHODS

General Polymerization Procedure

A standard experimental procedure was applied for all preparations of poly(amide-acids). The reaction medium was THF (HPLC grade, Burdick & Jackson Laboratories) and was stored under a nitrogen atmosphere over molecular sieves (0.3 nm effective pore size). Measured volumes of THF were transferred by nitrogen pressure from the storage vessel into a nitrogen purged resin kettle equipped with a water jacket and a three neck cover providing access for nitrogen, stirrer, and solvent. Contamination from stopcock grease was avoided by using Teflon sleeves on all glass joints and Teflon needle valves.

THF was added to a weighed amount of diamine in the nitrogen purged resin kettle. After dissolution of the diamine, a stoichiometric quantity of dianhydride was added. The reaction temperature was regulated by a circulating thermostated water bath connected to the jacket of the reaction kettle.

The temperature program depended on the reactivity of the diamine. With very reactive diamines, e.g., N-I or C-IX, the reactions were started at about 0°C (ice water cooling) and the final temperature did not exceed 40°C. Slowly reacting diamines, e.g., F-I, Cl-IV, and Cl-V, required prolonged heating close to the boiling point of THF. All reactions were vigorously stirred.

The resulting poly(amide-acid) was isolated after addition of chloroform to the reaction mixture. The polymer was allowed to settle and was then filtered through Teflon coated glass fiber filters. It was then transferred to extraction thimbles and extracted with diethyl ether in a Soxhlet for 16-18 h. The extracted and ether-free poly(amide-acid) was ground to particles of about 500 μm diameter, which were then thermally dehydrated to the polyimide form.

Cyclodehydration was performed under a vacuum of about 1 Pa in a rotary evaporator at about 30 rpm. The flask containing the polymer was heated in a silicone oil bath and was equipped with baffles to assure thorough mixing and

Table 7. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC DIANHYDRIDE AND DIFFERENT AROMATIC DIAMINES

Polyimide number	Diamine code	Diamine
PI-101	F-I	Tetrafluoro-*m*-phenylene diamine
PI-102	Cℓ-VI	α,α'-Diaminotetrachloro-*p*-xylene
PI-103	Cℓ-I	4-Chloro-*m*-phenylene diamine
PI-104	Cℓ-IV	Bis(4-amino-3-chlorophenyl)methane
PI-105	C-V	2,6-Diaminotoluene
PI-106	N-I	4-Azo-dianiline
PI-107	Cℓ-V	2,2',5,5'-Tetrachlorodiphenyldiamine
PI-108	Cℓ-IV	Bis(4-amino-3-chlorophenyl)methane
PI-109	C-IX	3,3',5,5'-Tetramethylbenzidine
PI-110	F-II	Octafluorobenzidine
PI-111	N-II	2,6-Diaminopyridine
PI-112	S-V	Bis(4-aminophneyl)sulfide
PI-113	Cℓ-V	2,2',5,5'-Tetrachlorodiphenyl
PI-114	F-I	Tetrafluoro-*m*-phenylene diamine
PI-115	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-116	S-II	Bis(3-aminophenyl)sulfone
PI-117	N-II	2,6-Diaminopyridine
PI-118	F-IV	Tetrafluoro-*p*-phenylene diamine
PI-119	S-I	Bis(4-aminophenyl)sulfone
PI-120	O-III	Bis(4-aminophenyl)ether
PI-121	Cℓ-III	4,4'-Diamino-3,3'-dichlorodiphenyl
PI-122	C-X	1,5-Diminonaphthalene
PI-123	C-XIII	1,2-Bis(4-aminophenyl)ethane
PI-124	Cℓ-VII	2-Chloro-*p*-phenylene diamine
PI-125	S-III	4,4'-Diaminodiphenylmethane-2,2'-sulfone
PI-126	F-III	3-Trifluoromethyl-*m*-phenylene diamine
PI-127	N-IV	3,6-Diamino-2,7-dimethylacridine
PI-128	C-VII	Tetramethyl-*p*-phenylene diamine
PI-129	N-V	2,5-Diaminopyridine
PI-130	N-VI	4,6-Diaminopyrimidine

(continued)

Table 7 (cont'd.)

Polyimide number	Diamine code	Diamine
PI-131	O-V	3,3'-Diaminobenzophenone
PI-132	N-III	3,6-Diaminoacridine
PI-133	O-VI	1,4-Diaminoanthraquinone
PI-134	C-VIII	*o*-Toluidine
PI-135	O-IV	2,6-Diaminoanthraquinone
PI-136	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-137	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-138	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-139	Cℓ-VII	2-Chloro-*p*-phenylene diamine
PI-140	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-141	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-142	C-XIV	4,4'-Ethylene-*m*-toluidine
PI-143	C-I	*p*-Phenylene diamine
PI-144	C-II	*m*-Phenylene diamine
PI-145	Cℓ-VII	2-Chloro-*p*-phenylene diamine
PI-146	C-IV	2,4-Diaminotoluene
PI-147	C-VI	2,4-Diaminocumene
PI-148	S-VII	Bis(2-aminophenyl)disulfide
PI-149	C-XI	Bis(4-aminophenyl)methane
PI-150	C-XII	Bis(3-aminophenyl)methane
PI-151	F-II	Octafluorobenzidine
PI-152	C-III	2,5-Diaminotoluene
PI-153	C-XV	4,4'-Diaminostilbene
PI-154	S-I	Bis(4-aminophenyl)sulfone
PI-155	C-XVI	α,α'-Diamino-*m*-xylene
PI-156	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-157	S-I	Bis(4-aminophenyl)sulfone
PI-158	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-159	S-I	Bis(4-aminophenyl)sulfone
PI-160	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-161	Cℓ-VII	2-Chloro-*p*-phenylene diamine
PI-162	Cℓ-VII	2-Chloro-*p*-phenylene diamine

(continued)

Table 7 (cont'd.)

Polyimide number	Diamine code	Diamine
PI-163	Cℓ-II	2,6-Dichloro-p-phenylene diamine
PI-164	C-IX	3,3',5,5'-Tetramethylbenzidine
PI-165	N-I	4-Azo-dianiline
PI-166	C-IX	3,3',5,5'-Tetramethylbenzidine
PI-167	N-I	4-Azo-dianiline
PI-168	N-I	4-Azo-dianiline
PI-169	N-VI	4,6-Diaminopyrimidine
PI-170	C-IX	3,3',5,5'-Tetramethylbenzidine
PI-171	N-VI	4,6-Diaminopyrimidine
PI-172	N-VI	4,6-Diaminopyrimidine
PI-173	N-VI	4,6-Diaminopyrimidine

Table 8. POLYIMIDE SORBENTS PREPARED FROM BENZOPHENONE TETRACARBOXYLIC DIANHYDRIDE AND DIFFERENT AROMATIC DIAMINES

Polyimide number	Diamine code	Diamine
PI-201	Cℓ-I	4-Chloro-*m*-phenylene diamine
PI-202	F-I	Tetrafluoro-*m*-phenylene diamine
PI-203	C-IX	3,3',5,5'-Tetramethylbenzidine
PI-204	N-I	4-Azo-dianiline
PI-205	Cℓ-IV	Bis(4-amino-3-chlorophenyl)methane
PI-206	Cℓ-V	2,2',5,5'-Tetrachlorodiphenyl
PI-207	N-II	2,6-Diaminopyridine
PI-208	Cℓ-II	2,6-Dichloro-*p*-phenylene diamine
PI-209	S-I	Bis(4-aminophenyl)sulfone
PI-210	S-II	Bis(3-aminophenyl)sulfone
PI-211	O-III	Bis(4-aminophenyl)ether
PI-212	S-V	Bis(4-aminophenyl)sulfide
PI-213	Cℓ-III	4,4'-Diamino-3,3'-dichlorodiphenyl
PI-214	C-X	1,5-Diaminonaphthalene
PI-215	C-V	2,6-Diaminotoluene
PI-216	Cℓ-VII	2-Chloro-*p*-phenylene diamine
PI-217	S-III	4,4'Diaminodiphenylmethane-2,2'-sulfone
PI-218	N-VI	2,4-Diaminopyrimidine
PI-219	N-III	3,6-Diaminoacridine

even heating of the powder. Pyrolysis of the silicone oil limited the maximum obtainable temperature to about 220-230°C.

After dehydration, the final polyimide was separated by sieving into three fractions designated A, B, and C which represent particle size ranges of 200-500, 100-200, and below 100 μm, respectively.

Viscosity Determination

The poly(amide-acids) were characterized by their inherent viscosities in dimethyl acetamide (DMA) at 30°C. Determinations were performed after ether extraction at concentrations close to 0.5 deciliters/gram (dl/g).

Inherent viscosities were converted to weight average molecular weights utilizing the relationship:

$$M_w = 4.42 \times 10^4 \, [\eta]^{1.28} \qquad (5\text{-}1)$$

given by Sroog[1] for poly(amide-acids) derived from PMDA and bis(4-aminophenyl) ether. Because of the large differences in chain stiffness between poly(amide-acids) derived from different diamines, the reported molecular weights can be considered only as first approximations.

Materials

Both dianhydrides, PMDA and BTDA, were purified by recrystallization from acetic anhydride and subsequent drying at ambient temperature at 0.7 Pa for 16-18 h. Further handling of the dianhydrides was performed inside a glove bag.

Discolored diamines were recrystallized from methanol and vacuum dried. Diamines received in salt form were converted into the free amines either by treatment with ion exchangers or by addition of stoichiometric amounts of sodium bicarbonate. Further purification was by recrystallization and/or sublimation.

A detailed purity analysis by differential scanning calorimetry (DSC) was performed on three diamines (Cl-II, Cl-VII, and S-I), which were used for large batch preparations of sorbents. Both chlorine-containing diamines were sublimed whereas, S-I was used as received but vacuum dried.

Purity determination was based on the melting point depression, T_o-T_m, as given by the van't Hoff equation

$$T_o - T_m = RT_o^2 \, x_2/\Delta H_f \qquad (5\text{-}2)$$

where ΔH_f is the molar enthalpy of fusion (cal/mol), R is the gas constant (1.987 cal $mol^{-1}K^{-1}$), T_o and T_m are the melting temperatures of pure and impure material, respectively, and x_2 is the mol fraction of impurity. The fraction, f, of the sample which is melted at sample temperature, T_s, is given by

$$f = (T_o - T_m)/(T_o - T_s) \qquad (5\text{-}3)$$

Combining both equations one obtains

$$T_s = T_o - (RT_o^2\, x_2/f\Delta H_f) \qquad (5\text{-}4)$$

Consequently, the mol fraction of impurity, x_2, can be calculated from the slope of a plot of T_s vs. 1/f.

The DSC scan of diamine Cℓ-VII is shown in Figure 1 and indicates the weight fractions melted at different points of the trace. The corresponding sample temperatures have to be corrected for the thermal lag inherent to the system by extrapolating to the baseline with the low temperature slope of the indium melting peak obtained under identical experimental conditions. Numerical values of the evaluation of the DSC scan are summarized in Table 9.

In Figure 2 sample temperatures are plotted versus weight fractions of melted material (open circles). Generally, curvature is observed unless the purity of the sample exceeds 99.99 mol %. This is a consequence of an increased melting range where the onset of melting is difficult to observe. Consequently, a correction has to be applied accounting for the premelting contribution. Figure 2 reveals that the data can be linearized by the addition of 1.5% of the enthalpy of fusion to each weight fraction of melted material (full circles).

Pertinent data for the purity determination by DSC of diamine Cℓ-VII are presented in Table 10, which also includes data for both additional diamines used for large batch preparations. All three of the diamines were found to be better than 99.9 mol-% pure.

RESULTS AND DISCUSSION

Polyimides from Fluorinated Diamines

The structures of the four commercially available fluorinated diamines are shown in Table 1. All of the diamines were used as received. Pertinent data for the prepared sorbents are summarized in Table 11.

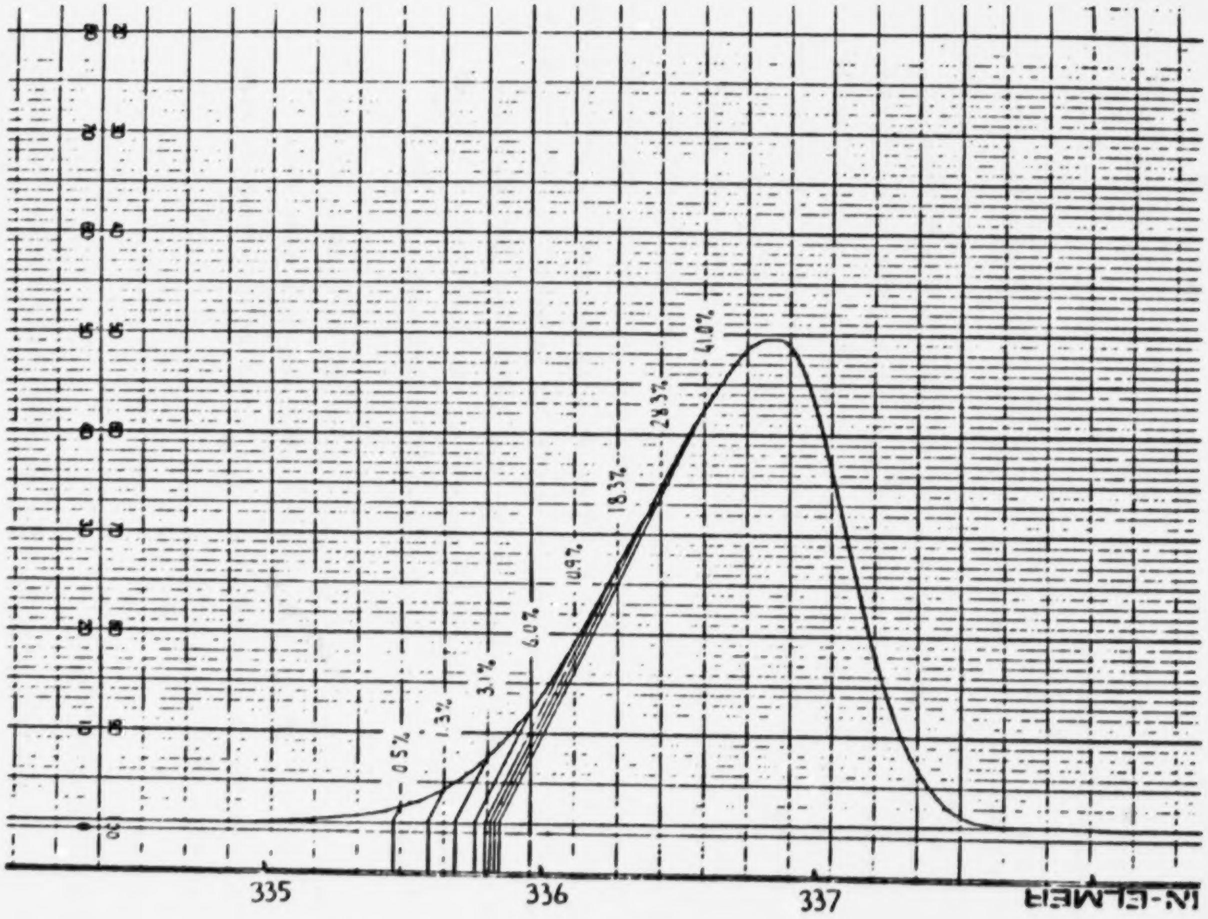


Figure 1. DSC scan of 5-chloro-p-phenylene diamine (Cℓ-VII) for purity determination. Accompanying numbers indicate weight percent of melted material.

Table 9. EVALUATION OF DSC SCAN OF 5-CHLORO-P-PHENYLENE DIAMINE (Cℓ-VIII)[a]

Temperature (K)	Wt. Fraction Melted	Reciprocal Wt. Fraction	Reciprocal Wt. Fraction Corrected by 1.5% of ΔH_f
335.46	0.005	196.6	50.5
335.59	0.013	79.2	36.7
335.69	0.031	32.2	22.0
335.77	0.060	16.5	13.4
335.80	0.109	9.1	8.2
335.81	0.183	5.5	5.1
335.82	0.283	3.5	3.4
335.85	0.410	2.4	2.4

[a] For graphic display of data see Figures 1 and 2.

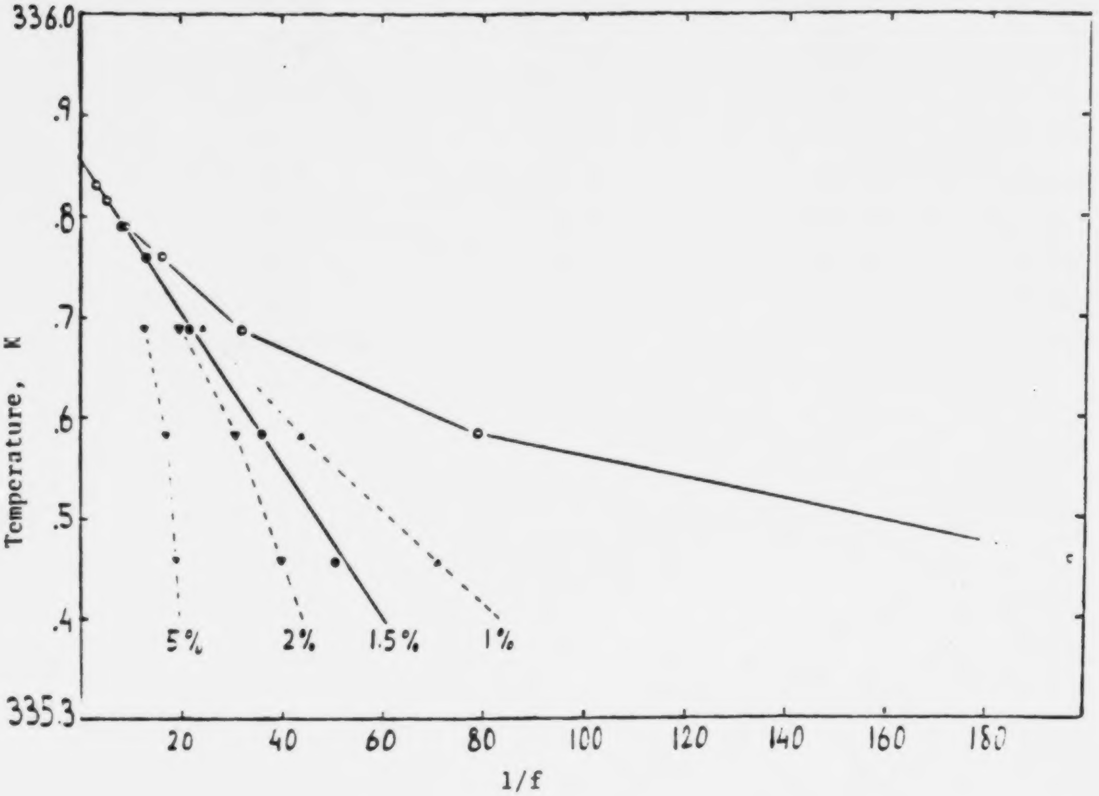


Figure 2. Evaluation of the DSC trace of Figure 1 according to eqn. (4). Accompanying numbers indicate % correction applied.

Table 10. EVALUATION OF DSC SCANS OF THREE DIAMINES FOR PURITY DETERMINATION[a]

Diamine Code	Cℓ-II	Cℓ-VII	S-I
Sample Weight (mg)	2.6	2.1	2.2
Melting Point, T_o (K)	396.22	335.86	448.00
Enthalpy of Fusion, ΔH_f (cal/mol)	5,660	3,980	5,350
Slope (eqn. 4)	0.0191	0.0078	0.0588
% Correction of ΔH_f	1.5	1.5	5.0
Mol Fraction Impurity, x_2	0.00035	0.00014	0.00079
Purity (mol. %)	99.96	99.98	99.92

[a] Scanning Conditions: Heating Rate = 2.5°/min
Range = 5 mcal/sec
Chart Speed = 16 cm/min

Table 11. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC (PI-1XX) OR BENZOPHENONE TETRACARBOXYLIC (PI-2XX) DIANHYDRIDE AND FLUORINATED AROMATIC DIAMINES

Polyimide Number	Diamine Code	Poly(amide-acid)		% Overall Yield After Sieving	% Yield of Size Fractions		
		Inherent Viscosity	Estimated M.W.		A	B	C
PI-101	F-I	0.09	2,000	89.5	60.9	25.9	2.7
PI-110	F-II	0.05	950	4.6	-	-	-
PI-114	F-I	0.11	2,700	69.6	49.3	16.4	3.9
PI-118	F-IV	0.09	2,000	42.4	21.5	14.4	6.5
PI-126	F-III	0.28	9,000	75.6	47.6	17.0	11.0
PI-151	F-II	0.01	-	[a]	-	-	-
PI-202	F-I	0.09	2,000	48.6	19.0	18.5	11.1

[a] Product sublimed during dehydration step.

Fluorine substitution of the aromatic ring strongly decreases the reactivity of the amine groups. Elevated reaction temperatures were required to produce low molecular weight polymers. Diamine F-II hardly polymerized at all and yielded only small amounts of waxy products in two attempts. Diamine F-III with fluorine substitution in the methyl group resulted in a somewhat higher molecular weight product with about 75% conversion.

Polyimides from Chlorinated Diamines

Structures of the chlorinated diamines utilized for sorbent preparations are presented in Table 2. In Table 12, pertinent data of the prepared polyimide sorbents are summarized.

Polyimide PI-102/Cℓ-VI showed low temperature stability due to the methylene groups adjacent to the imide groups. The corresponding polyimide based on BTDA was consequently not prepared.

Sample PI-208/Cℓ-II melted at about 220°C during the dehydration step. Both samples, PI-213/Cℓ-III and PI-216/Cℓ-VII were extremely hard particles. Only the former sample could be partially ground in a micromill.

Polyimides from Nitrogen-Containing Diamines

The structures of the six nitrogen-containing diamines used for polyimide preparation are shown in Table 3. With the exception of N-I and N-II, the diamines were received in salt form and had to be converted to free diamine. Pertinent data for the prepared polyimides are summarized in Table 13.

All of the diamines containing a nitrogen in the ring formed low molecular weight polymers with relatively low yields. The inherent viscosities of these polymers in the amide-acid form did not exceed 0.1 dl/g in DMA. Diamine N-IV yielded only an addition product which was soluble in dilute HCl (1:1). High molecular weight polymer was obtained in good yield with N-I, which contained the nitrogen in form of an azo-group.

Polyimides from Sulfur Containing Diamines

Structures of sulfur-containing diamines are shown in Table 4. Polyimides were prepared in THF from diamines containing S-S bridges and were found to be susceptible to ozone attack. Polyimides derived from the remaining diamines of Table 4 are summarized in Table 14.

The poly(amide-acid) of preparation PI-112/S-V crosslinked during ether extraction and became insoluble in DMA. Polyimide PI-212/S-V was extremely hard and could only be partially ground.

Table 12. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC (PI-1XX) OR BENZOPHENONE TETRACARBOXYLIC (PI-2XX) DIANHYDRIDE AND CHLORINATED AROMATIC DIAMINES

Polyimide Number	Diamine Code	Poly(amide-acid)		% Overall Yield After Sieving	% Yield of Size Fractions		
		Inherent Viscosity	Estimated M.W.		A	B	C
PI-102	Cℓ-VI	0.23	6,700	88.7	81.6	5.9	1.2
PI-103	Cℓ-I	0.17	4,700	93.8	46.2	35.5	12.1
PI-104	Cℓ-IV	0.14	3,600	82.0	51.4	18.6	12.0
PI-107	Cℓ-V	0.16	4,000	18.2	10.7	5.3	2.2
PI-108	Cℓ-IV	0.45	15,600	83.3	49.2	22.3	11.7
PI-113	Cℓ-V	0.14	3,600	55.2	21.3	23.4	10.5
PI-115	Cℓ-II	0.09	2,000	53.3	32.7	18.1	2.6
PI-121	Cℓ-III	0.47	16,700	71.6	38.5	14.9	15.4
PI-124	Cℓ-VII	0.46	16,300	81.7	47.0	24.9	9.8
PI-201	Cℓ-I	0.31	10,000	93.4	48.0	21.6	23.9
PI-205	Cℓ-IV	0.41	14,000	78.6	52.8	19.2	6.6
PI-206	Cℓ-V	0.24	7,000	47.4	30.7	12.0	4.7
PI-208	Cℓ-II	0.07	1,500	[a]	-	-	-
PI-213	Cℓ-III	0.29	9,000	65.9	[b]	[b]	[b]
PI-216	Cℓ-VII	0.52	19,000	[c]	-	-	-

[a] Polymer melted during dehydration step at 200-230°C.

[b] Very hard polymer, could not be completely ground in micromill.

[c] Very hard polymer, could not be broken up.

Table 13. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC (PI-1XX) OR BENZOPHENONE TETRACARBOXYLIC (PI-2XX) DIANHYDRIDE AND NITROGEN-CONTAINING AROMATIC DIAMINES

Polyimide number	Diamine code	Poly(amine-acid)		% Overall yield after sieving	% Yield of size fractions		
		Inherent viscosity	Estimated M.W.		A	B	C
PI-106	N-I	0.72	29,000	92.2	27.2	32.1	33.2
PI-111	N-II	0.057	1,100	50.3	24.4	18.2	7.7
PI-117	N-II	0.062	1,300	43.4	27.8	12.4	3.3
PI-127	N-IV	0.031	500	53.4	22.5	25.0	6.4
PI-129	N-V	0.062	1,300	55.6	39.0	14.9	1.7
PI-130	N-VI	0.066	1,400	60.1	5.5	10.9	43.7
PI-132	N-III	0.065	1,400	62.6	52.0	9.9	0.7
PI-204	N-I	0.60	23,000	89.1	57.4	19.7	3.0
PI-207	N-II	0.090	2,000	65.8	34.1	30.0	1.7
PI-218	N-VI	0.093	2,100	24.1	4.5	6.2	13.5
PI-219	N-III	0.060	1,200	a	30.3	a	a

a = Very large losses of fine powder.

Table 14. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC (PI-1XX) OR BENZOPHENONE TETRACARBOXYLIC (PI-2XX) DIANHYDRIDE AND SULFUR-CONTAINING AROMATIC DIAMINES

Polyimide Number	Diamine Code	Poly(amide-acid)		% Overall Yield After Sieving	% Yield of Size Fractions		
		Inherent Viscosity	Estimated M.W.		A	B	C
PI-112	S-V	a	a	83.7	56.6	21.7	5.3
PI-116	S-II	0.25	7,500	85.9	48.1	33.8	4.0
PI-119	S-I	0.18	4,900	81.7	49.4	27.1	5.1
PI-125	S-III	0.52	19,000	83.8	21.3	51.4	11.1
PI-148	S-VII	0.14	3,500	38.1	24.6	10.9	2.5
PI-209	S-I	0.25	7,500	73.4	20.9	37.8	14.6
PI-210	S-II	0.24	7,100	65.1	57.5	6.3	1.3
PI-212	S-V	0.24	7,100	69.9	b	b	b
PI-217	S-III	0.40	13,600	88.9	55.5	14.5	19.0

[a] Polymer insoluble after ether extraction.
[b] Very hard polymer, could not be ground completely.

Polyimides from Oxygen Containing Diamines

The structures of six commercially available aromatic diamines containing oxygen are presented in Table 5. Two of the diamines, O-I and O-II, were not used in the present work since previous results revealed insufficient thermal stability for methoxygroup-containing polyimides. Pertinent data for the polymerizations performed are summarized in Table 15.

Both diaminoanthraquinones, O-IV and O-VI, yielded poor results. Low molecular weight polymer was obtained in low yield from O-VI, and no polymer could be isolated from an attempted polymerization of O-IV.

Diamines O-III and O-V produced fair yields of polymers of medium molecular weights. Polymerization conditions of O-III would require modifications to increase the yield of useful particle size (Range A, 200-500 μm).

Polyimides from Diamines Without Heteroatoms

Structures of 17 commercially available aromatic diamines without heteroatoms are shown in Table 6. Pertinent data for polyimides prepared are summarized in Table 16.

Polymers prepared with PMDA were obtained in good yields (80-90 percent after sieving). The molecular weights were relatively low, which is very likely a consequence of the heterogeneous nature of polymerizations carried out in THF. Only slightly lower yields were obtained with BTDA (70-80 percent), but the polymers were of extremely small particle size (<100 μ). Improved yields in the desired range of 200-500 μm might be obtained by carrying out the polymerizations in the presence of small amounts of a triamine, e.g., 2,4,6-triaminotoluene, which acts as a cross-linking agent.

Diamine C-XVII was not included in the preparations because of the known low thermal stability of polyimides possessing aliphatic chain elements attached to the imide groups. One representative of this structural group diamine C-XVI was selected for polymerization.

Large Batch Preparations

Six polyimides were selected to be prepared in larger than previous amounts for detailed evaluation of their properties. The selected polyimides were formed from PMDA and the diamines Cℓ-II, Cℓ-VII, N-I, N-VI, S-I, and C-IX. Each of the polyimides was prepared in several batches to test the reproducibility of the polymerization process and to utilize existing equipment.

Table 15. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC (PI-1XX) OR BENZOPHENONE TETRACARBOXYLIC (PI-2XX) DIANHYDRIDE AND OXYGEN-CONTAINING AROMATIC DIAMINES

Polyimide number	Diamine code	Poly(amide-acid)		% Overall yield after sieving	% Yield of size fractions		
		Inherent viscosity	Estimated M.W.		A	B	C
PI-120	O-III	0.54	20,000	83.2	5.5	19.2	58.5
PI-131	O-V	0.51	19,600	59.8	31.4	10.3	5.7
PI-133	O-VI	0.090	2,000	12.9	8.4	4.1	0.4
PI-135	O-IV	a	a	a	a	a	a
PI-211	O-III	0.84	35,000	64.3	25.6	14.6	5.9

a = No polymer formed.

Table 16. POLYIMIDE SORBENTS PREPARED FROM PYROMELLITIC (PI-1XX) OR BENZOPHENONE TETRACARBOXYLIC (PI-2XX) DIANHYDRIDE AND AROMATIC DIAMINES WITHOUT HETEROATOMS

Polyimide number	Diamine code	Poly(amide-acid)		% Overall yield after sieving	% Yield of size fractions		
		Inherent viscosity	Estimated M.W.		A	B	C
PI-105	C-V	0.23	6,800	93.2	38.6	9.9	44.7
PI-109	C-IX	0.28	8,600	91.1	40.0	29.4	21.6
PI-122	C-X	0.20	5,600	87.0	23.1	9.7	54.3
PI-123	C-XIII	0.77	31,500	80.2	38.8	20.2	21.2
PI-128	C-VII	0.18	4,900	91.9	8.3	7.1	76.5
PI-134	C-VIII	0.42	14,500	78.7	15.6	8.0	55.1
PI-142	C-XIV	0.51	18,600	81.3	27.3	21.1	32.9
PI-143	C-I	0.23	6,700	88.0	42.5	27.4	18.1
PI-144	C-II	0.22	6,300	91.9	40.6	25.5	25.3
PI-146	C-IV	0.20	5,600	80.2	3.5	8.5	68.2
PI-147	C-VI	0.12	3,000	83.1	44.1	28.5	10.4
PI-149	C-XI	0.39	13,000	75.5	23.7	6.8	45.1
PI-150	C-XII	0.37	12,500	71.5	27.5	6.2	2.5
PI-152	C-III	0.28	8,500	82.2	56.5	18.4	7.3
PI-153	C-XV	0.47	17,000	84.0	55.2	19.4	3.3
PI-155	C-XVI	[a]	[a]	35.1	27.3	5.3	0.6
PI-203	C-IX	0.53	19,600	75.9	5.7	20.6	49.6
PI-214	C-X	0.30	9,400	71.5	2.3	1.5	67.6
PI-215	C-V	0.23	6,700	77.0	1.5	0.9	74.5

[a] Insoluble in DMA

2,6-Dichloro-p-phenylene Diamine (Cℓ-II)--

Polymerization conditions and polymer properties for this polyimide are summarized in Table 17.

The diamine was first purified by Soxhlet extraction with diethyl ether. The ether was removed in a rotary evaporater and the residue was recrystallized from methanol-water. The recrystallized product was finally purified by sublimation at 90°C. According to DSC analysis (Table 10) the pale yellow crystals were of 99.96 mol-% purity.

In spite of the high purity of the diamine, only low molecular weight polymers were obtained in low yields. This is a consequence of the unfavorable diamine structure with two chlorines adjacent to one amine group. Because extremely low molecular weight products were formed at low reaction temperatures, it was raised to refluxing THF in subsequent preparations.

5-Chloro-p-phenylene diamine (Cℓ-VII)--

Polymerization conditions and polymer properties for this polyimide are summarized in Table 18.

The diamine was received as the sulfate salt from which the free diamine was obtained by the addition of KOH to the aqueous solution of the salt. The free diamine was extracted with ether and the solvent was removed in a rotary evaporator. The residue was finally purified by sublimation at low temperature (m.p. = 63°C). According to DSC analysis (Table 10), the resulting white needles were of 99.98 mol-% purity. The free diamine is easily oxidized and discolors on prolonged exposure to air.

The diamine Cℓ-VII, possessing only one chlorine, polymerized under milder conditions than Cℓ-II. Polymers in an estimated molecular weight range of $10\text{-}16 \times 10^3$ were obtained at conversions of about 70-80%. About 50% of the total yield were of proper particle size (fraction A, 200-500 μm).

4,4'-Azo-dianiline (N-I)--

Polymerization conditions and polymer properties for this polyimide are summarized in Table 19.

The diamine was a pure product and was used as received. Polymerization of N-I proceeded rapidly to good conversions (80-90%). About 50% of the sieved products were of proper particle size (fraction A). The molecular weight is probably limited by the heterogeneous nature of the polymerization process.

Table 17. LARGE BATCH PREPARATION OF POLYIMIDE SORBENT FROM PMDA AND 2,6-DICHLORO-P-PHENYLENE DIAMINE (Cℓ-II)

Preparation No.	Total Solid (g)	THF (mL)	Polymerization (°C)	Polymerization (Hrs)	$CHCl_3$ (mL)	% Polyimide Yield Size Fraction A	B	C	Total	Inherent Viscosity before extraction	Inherent Viscosity after extraction	M_v Estimated	Size Fraction A (g)
115	15.3	150	58	9	800	32.7	18.1	2.6	53.3	0.095	0.089	1,990	4.5
136	22.8	200	22	1	500	24.2	11.7	1.8	37.7	0.025	0.023	350	5.0
137	16.8	150	0	3	850	29.6	18.1	3.5	51.2	0.040	0.041	740	4.5
138	16.9	300	58	18	500	44.2	19.0	7.5	70.7	0.115	0.127	3,140	6.8
140	39.1	1,100	Reflux	29	3,000	29.5	12.1	4.6	46.1	0.113	0.093	2,090	10.5
141	70.4	1,500	"	20	2,000	40.0	12.9	16.9	69.8	0.098	0.112	2,670	25.6
156	57.1	900	"	16	1,900	33.2	12.4	3.2	48.8	0.078	0.083	1,820	17.3
158	42.1	800	"	21	3,000	20.8	5.1	1.3	27.3	0.072	0.074	1,570	8.0
160	57.4	900	"	19	3,000	10.8	4.9	1.4	17.1	0.093	0.074	1,570	5.7
163	62.5	1,100	"	23	3,000	13.7	5.2	3.1	22.0	0.068	0.091	2,050	7.8

Table 18. LARGE BATCH PREPARATION OF POLYIMIDE SORBENT FROM PMDA AND 5-CHLORO-P-PHENYLENE DIAMINE (Cℓ-VII)

Preparation No.	Total Solid (g)	THF (mL)	Polymerization (°C)	Polymerization (Hrs)	$CHCl_3$ (mL)	% Polyimide Yield Size Fraction A	% Polyimide Yield Size Fraction B	% Polyimide Yield Size Fraction C	% Polyimide Yield Total	Inherent Viscosity before extraction	Inherent Viscosity after extraction	M_v Estimated	Size Fraction A (g)
124	19.3	200	45	1	500	47.0	24.9	9.8	81.7	0.411	0.463	16,400	8.2
139	19.3	200	49	0.5	900	48.8	19.0	4.8	72.6	0.430	0.451	15,800	8.5
145	44.7	500	50	0.5	900	46.2	15.6	4.9	66.6	0.305	0.334	10,800	18.6
161	51.9	600	58	2	600	52.3	24.7	6.5	83.4	0.315	0.240	9,000	24.4
162	33.9	500	58	2	600	51.8	18.5	4.1	74.4	0.316	0.299	9,400	15.8

Table 19. LARGE BATCH PREPARATION OF POLYIMIDE SORBENT FROM PMDA AND 4,4'-AZO-DIANILINE (N-I)

Preparation No.	Total Solid (g)	THF (mL)	Polymerization (°C)	Polymerization (Hrs)	$CHCl_3$ (mL)	% Polyimide Yield Size Fraction A	B	C	Total	Inherent Viscosity before extraction	Inherent Viscosity after extraction	M_v Estimated	Size Fraction A (g)
106	17.9	200	40	3	-	27.2	32.1	33.2	92.4	-	0.72	29,000	4.5
165	48.6	600	59	2	500	49.5	20.4	18.0	87.9	0.47	0.42	14,700	22.0
167	51.3	650	58	1	500[a]	52.2	25.3	11.7	89.2	0.59	0.47	16,900	24.6
168	60.8	700	59	1	500[a]	57.5	13.6	8.7	79.9	0.69	0.67	26,500	32.0

[a] Diethylether.

4,6-Diaminopyrimidine (N-VI)--

Polymerization conditions and polymer properties for this polyimide are summarized in Table 20.

The diamine was received as the hemisulfate salt from which the free diamine was obtained by addition of a stoichiometric amount of KOH to the aqueous solution of the salt. After evaporation to dryness, the diamine was extracted with dry methanol and finally purified by sublimation.

Only low molecular weight polymers of N-VI were formed; conversion was about 50%. Most of the polymer was in the form of fine powder, further decreasing the yield of useful product.

Bis(4-aminophenyl)sulfone (S-I)--

Polymerization conditions and polymer properties for this polyimide are summarized in Table 21.

The diamine was a pure product which was used as received after drying under vacuum. Bis(4-aminophenyl)sulfone (S-I) converted to low molecular weight polymer in good yields (70-80%) with 60-70% of the total yield being of proper particle size. Even in DMA, where the polymerization proceeds homogeneously, diamine S-I is known to yield polymers with inherent viscosities not exceeding 0.5 dl/g. It is, therefore, not surprising that lower molecular weight products result from heterogeneous reaction conditions in THF.

3,3',5,5'-Tetramethylbenzidine (C-IX)--

Polymerization conditions and polymer properties for this polyimide are summarized in Table 22.

The diamine was a very pure product which was used as received. Polymerizations proceeded rapidly and were started with ice-water cooling to prevent overheating. With one exception (PI-164), the conversions were close to 100%. The estimated molecular weights were around 5,000 and were very likely limited by the heterogeneous polymerization conditions.

SUMMARY

Forty-two different aromatic diamines were selected from a list of 47 commercially available compounds and reacted with PMDA to form polyimide sorbents. The diamines excluded were those which were known to yield unstable products. Polyimides containing -S-S- bridges are severely attacked by ozone and polyimides containing methoxy groups are of insufficient thermal stability.

Table 20. LARGE BATCH PREPARATION OF POLYIMIDE SORBENT FROM PMDA AND 4,6-DIAMINOPYRIMIDINE (N-VI)

Preparation No.	Total Solid (g)	THF (mL)	Polymerization (°C)	Polymerization (Hrs)	$CHCl_3$ (mL)	% Polyimide Yield Size Fraction A	B	C	Total	Inherent Viscosity before extraction	Inherent Viscosity after extraction	M_v Estimated	Size Fraction A (g)
130	14.6	200	59	4	500	5.5	10.9	43.7	60.1	0.061	0.066	1,400	0.7
169	15.1	250	59	16	600[a]	29.4	9.6	17.7	56.6	0.049	0.051	980	3.4
171	34.1	500	59	22	700[a]	26.1	8.6	12.7	47.5	0.066	0.113	2,700	7.9
172	32.0	400	59	17	800[a]	7.3	4.9	37.4	49.6	0.058	0.085	1,900	2.1
173	65.0	1,500	68	22	1,000[a]	12.2	3.8	42.7	58.7	-	-	-	7.0

[a] Diethylether.

Table 21. LARGE BATCH PREPARATION OF POLYIMIDE SORBENT FROM PMDA AND BIS(4-AMINOPHENYL)SULFONE (S-I)

Preparation No.	Total Solid (g)	THF (mL)	Polymerization		$CHCl_3$ (mL)	% Polyimide Yield Size Fraction				Inherent Viscosity		M_v Estimated	Size Fraction A (g)
			(°C)	(Hrs)		A	B	C	Total	before extraction	after extraction		
119	24.3	300	58	2	500	49.4	27.1	5.1	81.7	0.162	0.178	4,800	11.0
153	52.5	600	58	1.3	600	51.6	15.0	4.5	71.0	0.147	0.156	4,100	25.0
157	65.6	700	58	2	700	48.8	21.5	6.4	76.7	0.150	0.149	3,900	29.6
159	47.3	600	58	2	700	46.5	21.6	7.1	75.2	0.175	-	4,700	20.3

Table 22. LARGE BATCH PREPARATION OF POLYIMIDE SORBENT FROM PMDA AND 3,3',5,5'-TETRAMETHYLBENZIDINE (C-IX)

Preparation No.	Total Solid (g)	THF (mL)	Polymerization (°C)	Polymerization (Hrs)	$CHCl_3$ (mL)	% Polyimide Yield Size Fraction A	B	C	Total	Inherent Viscosity before extraction	Inherent Viscosity after extraction	M_v Estimated	Size Fraction A (g)
109	23.3	150	42	1	-	40.0	29.4	21.6	91.1	-	0.28	8,600	8.6
164	18.9	150	59	1.5	500	44.5	13.3	1.0	58.8	0.175	0.173	4,700	7.8
166	34.7	250	59	1	500	22.8	9.6	64.5	96.9	0.183	0.188	5,200	7.3
170	48.2	400	59	18	800	52.7	22.6	21.8	97.1	0.201	-	5,600	23.4

Methylene groups attached to the imide group were found to decrease the softening point of the polymer and only two diamines yielding this structure were used in the preparations of sorbents.

Three preparations did not yield useful products. Octafluorobenzidine (F-II) yielded only waxy products in two polymerization attempts (PI-110 and 151). 2,6-Diaminoanthraquinone (O-IV) was nearly insoluble in THF and did not polymerize under these conditions (PI-135). 3,6-Diamino-2,7-dimethylacridine (N-IV) yielded extremely low molecular weight products (PI-127), which very likely corresponded to simple adducts of PMDA.

In addition to polyimides based on PMDA, 19 different polyimides were prepared from BTDA. The inferior properties of this structural variation were soon recognized, and further use of BTDA was discontinued.

Prepared quantities of polyimides generally did not exceed 10 g of size fraction A (200-500 µm) which were sufficient for screening purpose. Larger quantities (20-80 g) of six selected sorbents were prepared for extensive characterizations.

All polyimides derived from PMDA were characterized by thermogravimetric analysis (TGA). Results of these analyses are reported in Section 6.

SECTION 5

LEVEL I TESTING OF POLYIMIDE SORBENTS

INTRODUCTION

Subsequent to the synthesis of each polyimide discussed in Section 4, a Level I testing procedure was performed. The Level I testing procedure was a screening method which has been devised to sort the polymers according to specific, desirable properties. The tests which were employed under the Level I approach consisted of (a) thermal gravimetric analysis, (b) determining the background from the sorbent by programmed temperature gas chromatography, (c) determining retention volumes and theoretical plates for a set of test compounds under programmed temperature gas chromatography, and (d) determining the effect of humidity on retention volumes for a specially selected set of test compounds. Those polyimides which exhibited good performance characteristics according to these tests and were better than Tenax GC®, which is used as a reference, were selected for further examination. These were subjected to Level II testing. Thus, Level I testing was designed to eliminate sorbents with undesirable properties and to identify only those which exhibited more suitable properties for use as sorbents in the sampling of vapor-phase organics from ambient air.

EXPERIMENTAL PROCEDURES

Thermogravimetric Analysis

The thermal stabilities of forty polyimides derived from PMDA and different diamines were investigated by thermogravimetric analysis. The instrument used was a thermogravimetric system (Model TGS-2, Perkin-Elmer) in combination with a differential scanning calorimeter (Model DSC-2, Perkin-Elmer) which supplied the temperature program. Weight loss data were recorded on a strip-chart recorder (Model 56, Perkin-Elmer).

All analyses were performed in a helium atmosphere at a heating rate of 20 degrees/min. Chart speed was 5 mm/min. The polyimide samples were in the form of powders of size fraction A (200-500 μm) in amounts of 3-10 mg. The instrument was used in "% Sample Mode", i.e., the sample weight was set to full chart width (100 units) of the recorder and the weight loss was recorded in percent initial weight.

The instrument was calibrated for temperature accuracy by utilizing magnetic transition temperatures (Curie points) of four ferromagnetic standards.

Alumel	163°C
Nickel	354°C
Nicoseal Deep Draw	438°C
Perkalloy	596°C

Calibration conditions were identical to those applied for sample evaluation. A linear correlation was established between chart speed and heating rate.

Volatile Background of the Sorbents

Glass columns (0.914 m x 2 mm i.d.) were rinsed with 100 mL each of distilled water, methanol, and methylene chloride and dried under vacuum. The columns were filled with the sorbents (35/60 mesh) using tapping/suction. The columns were weighed before and after filling to determine the amount of polymer packing. The physical characteristics of the polymers were observed and recorded. After conditioning the columns overnight at 300°C under helium flow (20-25 mL/min), temperature programmed gas chromatography (GC) was performed using a detector sensitivity of 2×10^{-11} AFS.

Gas chromatographic parameters:

Instrument: Varian 1400 (FID)
Septum: Pyrosep with overnight thermal conditioning
Carrier gas: helium (20-25 mL/min)
Mass flow controller: Matheson Model 8240
Detector temperature: Flame ionization, 250°C
Injector temperature: 130-150°C
Temperature program: 50°C initial
50°C-275°C at 8°C/min

Retention Volumes for Test Substances in Temperature Programmed Gas Chromatography

Retention volumes for a group of test substances were determined using the GC parameters listed above. The test substances used are given in Table 23.

The GC parameters for determining water retention were as follow:

Instrument: Varian 3700

Carrier gas: helium (20-25 mL/min)

Injector temperature: 220°C

Detector: Thermal conductivity, 260°C

Filament temperature: 340°C

Oven temperature: 120°C isothermal

The test substances were injected as diluted (in air) vapors. Approximately 20 µL of the neat liquid was injected into a 125 mL Pierce vial sealed with Teflon lined rubber septa. Five and 50 µL samples of gas (Table 23) were removed from the vials with gas tight Hamilton syringes and injected onto the column containing the sorbent.

Survey of Theoretical Plates and Elution Temperatures

The retention times and base peak widths were measured on the chromatograms generated above. The theoretical plates (N) were calculated using the relationship:

$$N = 16 \times \left(\frac{t_R}{w}\right)^2$$

t_R = retention time of the peak, min
w = base width of the peak, min

Humidity Testing on Selected Sorbents

To simulate high humidity conditions, a wash bottle containing glass rings and distilled water was placed in line with the carrier gas and heated to approximately 30°C with heating tape. The test substances were applied to the columns in 50 µL volumes and the temperature programmed from 50°C to 275°C at 8°C/min. The retention volumes and approximate number of theoretical plates were determined.

Comparison of Retention Volumes on Tenax Columns

A Tenax GC® column was packed at the outset of this project to be used as a reference for the data obtained from other sorbents. Three to four months

Table 23. TEST SUBSTANCES EMPLOYED FOR DETERMINING RETENTION CHARACTERISTICS

Compound	B.P. (°C)	Amounts Injected[a]
Benzene	80.1	175 and 878
Ethanol	78.5	158 and 789
Methyl ethyl ketone	79.6	161 and 805
Nitromethane	100.8	227 and 1,137
Pyridine	115.5	196 and 982
C_7, C_8, C_9, C_{10} n-alkanes	98.4 125.7 150.8 174.1	146 and 730
Acetonitrile	81.6	157 and 786
1,2-Dichloroethane	83.5	247 and 1,235
Vinyl chloride	-13.37	182 and 910
Water	100	200 and 1,000

[a] 5 and 50 μL were injected containing these nanogram quantities.

later, a large void volume developed and another one was prepared. The test substances were injected onto both columns in 5μL and 50μL sample sizes and the differences in retention data noted.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Thermogravimetric analysis data of the investigated 40 polyimides are summarized in Table 24. The polymer samples were first conditioned by heating to 300°C and keeping them at this temperature for five minutes. After cooling the samples to 50°C, the instrument was reset to a sample weight of 100%, and the weight loss was recorded up to 700°C at a heating rate of 20°C/min. The recorded %-weight-loss traces of all samples are presented in Figures 3 to 8.

In Table 24, temperatures in °C are reported for both heating periods representing the onset of weight loss, i.e., the temperatures corresponding to the first discernible deviation of the recorder trace from the 100% line. Observed weight losses are then reported for the end of the conditioning period at 300°C as well as for three arbitrarily selected temperatures (400, 500, and 600°C) of the second heating period.

With few exceptions (six polyimide samples), the onset of weight loss for conditioned samples was found to be higher than 300°C. The majority of the polyimides possessed high temperature stability, exhibiting less than 2 and 5% weight loss at 400 to 500°C, respectively. At 600°C the weight losses exceeded 10% in most cases.

Volatile Background of the Sorbents

The general characteristics of the sorbents, as observed from the filling and conditioning of the columns, are listed in Tables A1 through A6.

For a few sorbents, problems developed at this early stage: for example, the particles of PI-219, PI-120, PI-134, and PI-122 were too soft to pack, and no further testing was performed. The formation of electrostatic charge on some sorbent granules makes packing the columns difficult, especially PI-124.

The apparent packing densities of the sorbents, as determined by dividing the weight of sorbents in the column by column volume, have a range of 0.115 g/mL to 0.863 g/mL, with the majority of values between 0.25 and 0.50 g/mL.

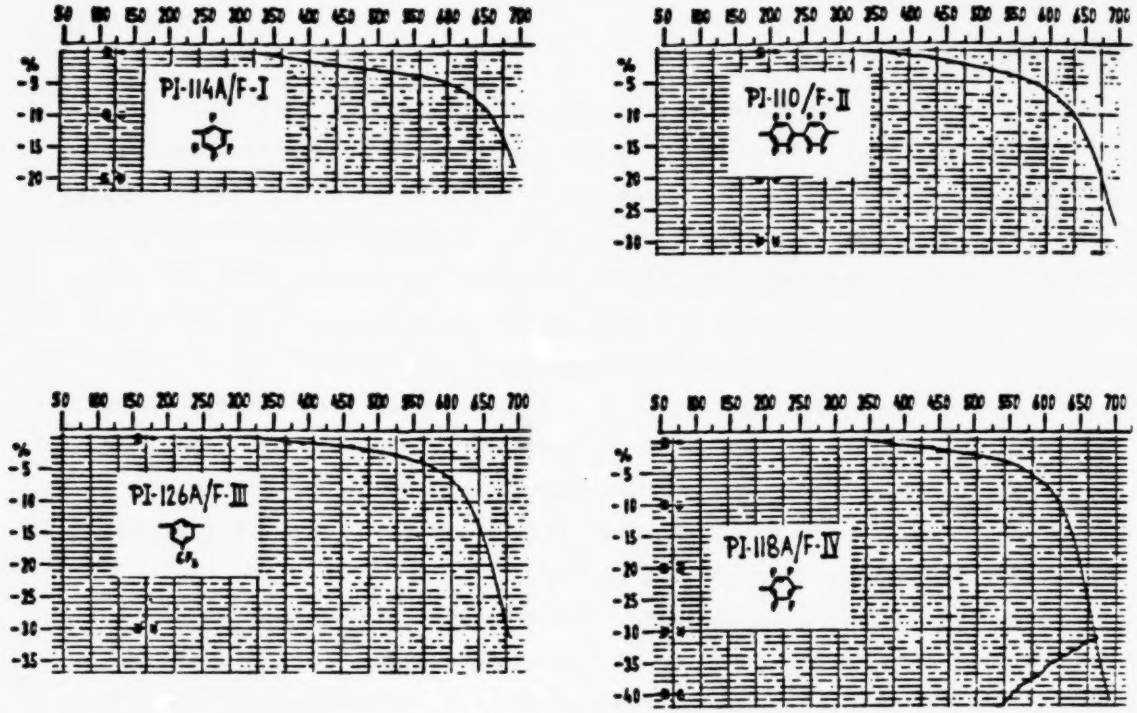


Figure 3. Thermogravimetric analysis of polyimides derived from fluorinated diamines.

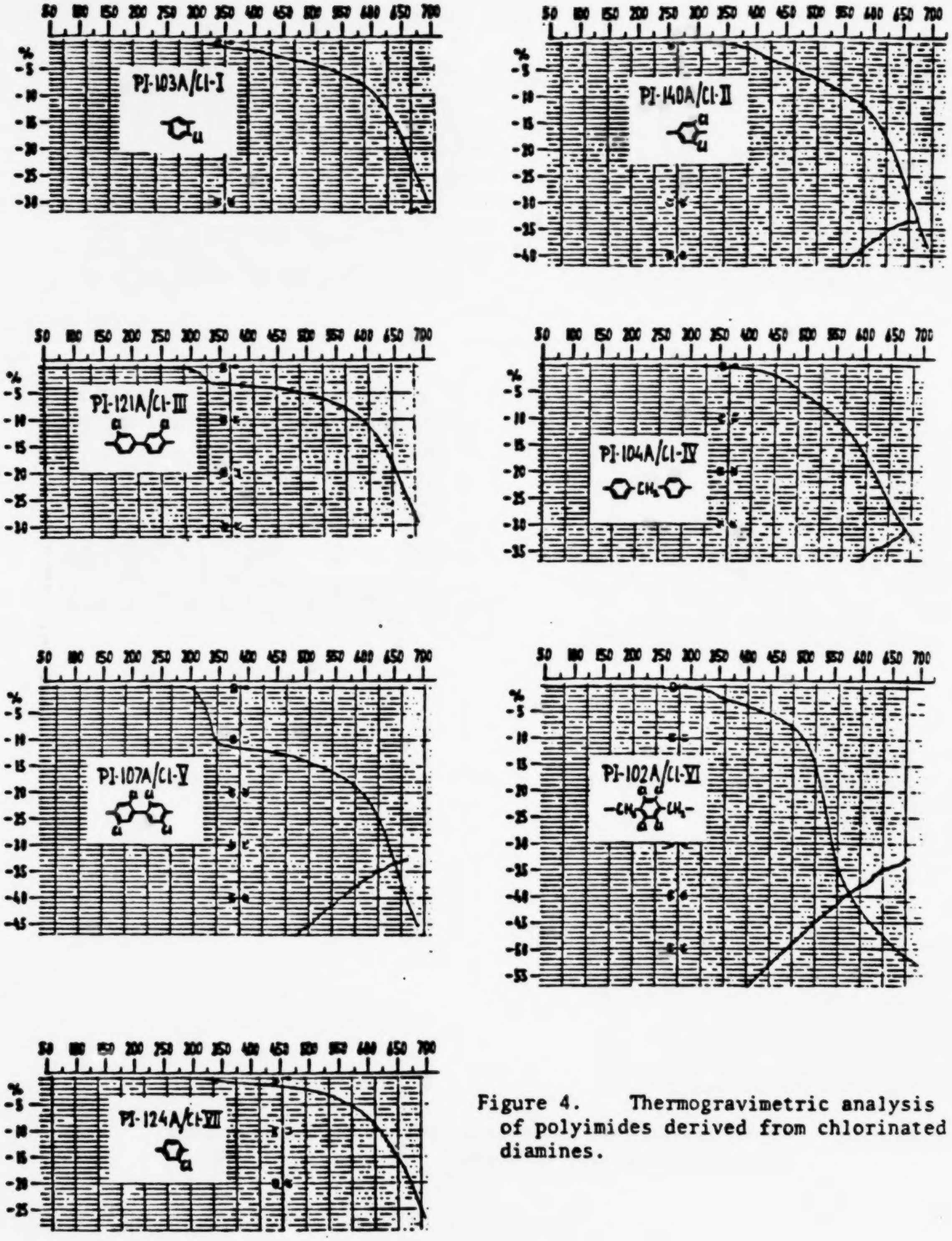


Figure 4. Thermogravimetric analysis of polyimides derived from chlorinated diamines.

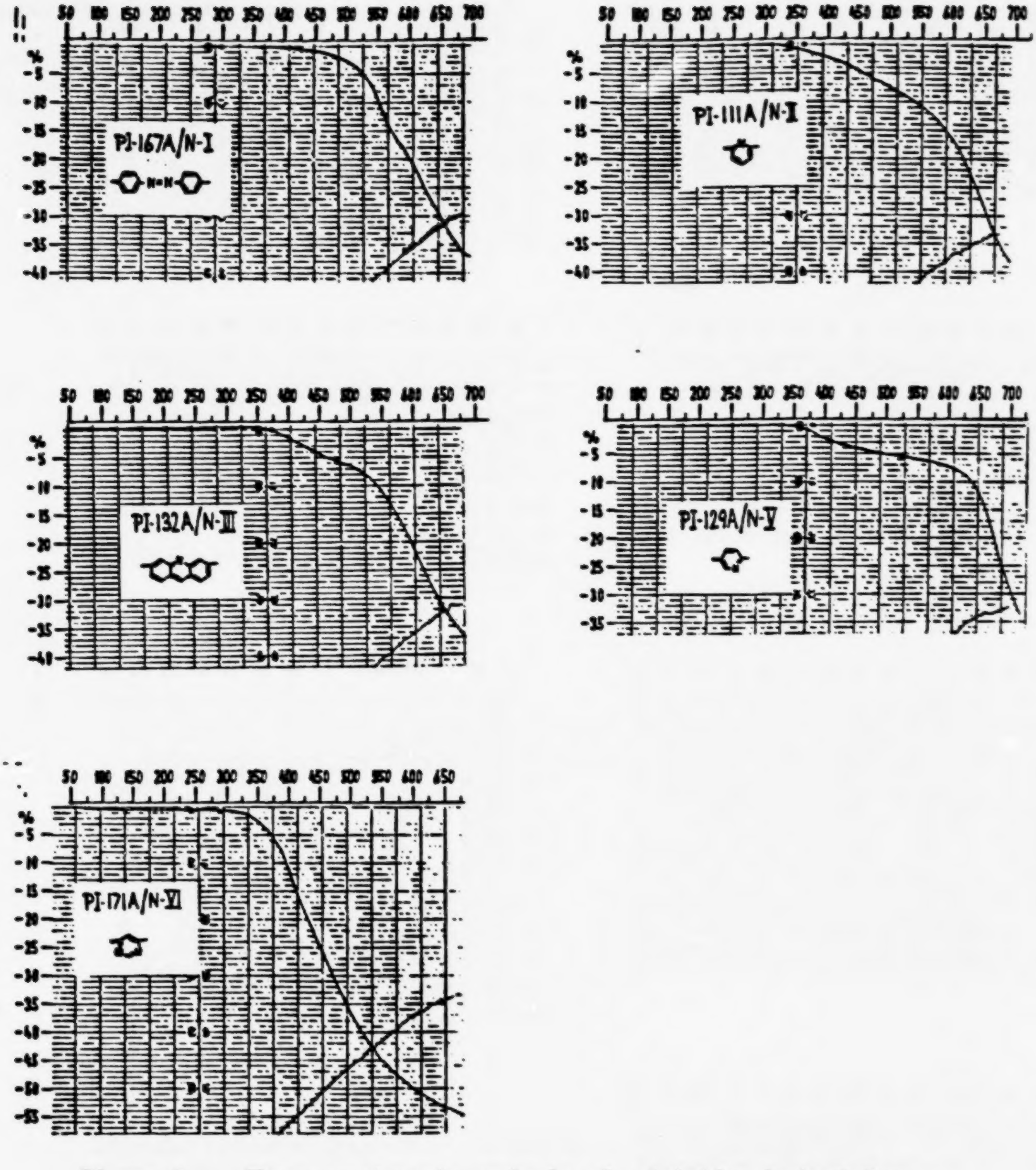


Figure 5. Thermogravimetric analysis of polyimides derived from diamines containing nitrogen.

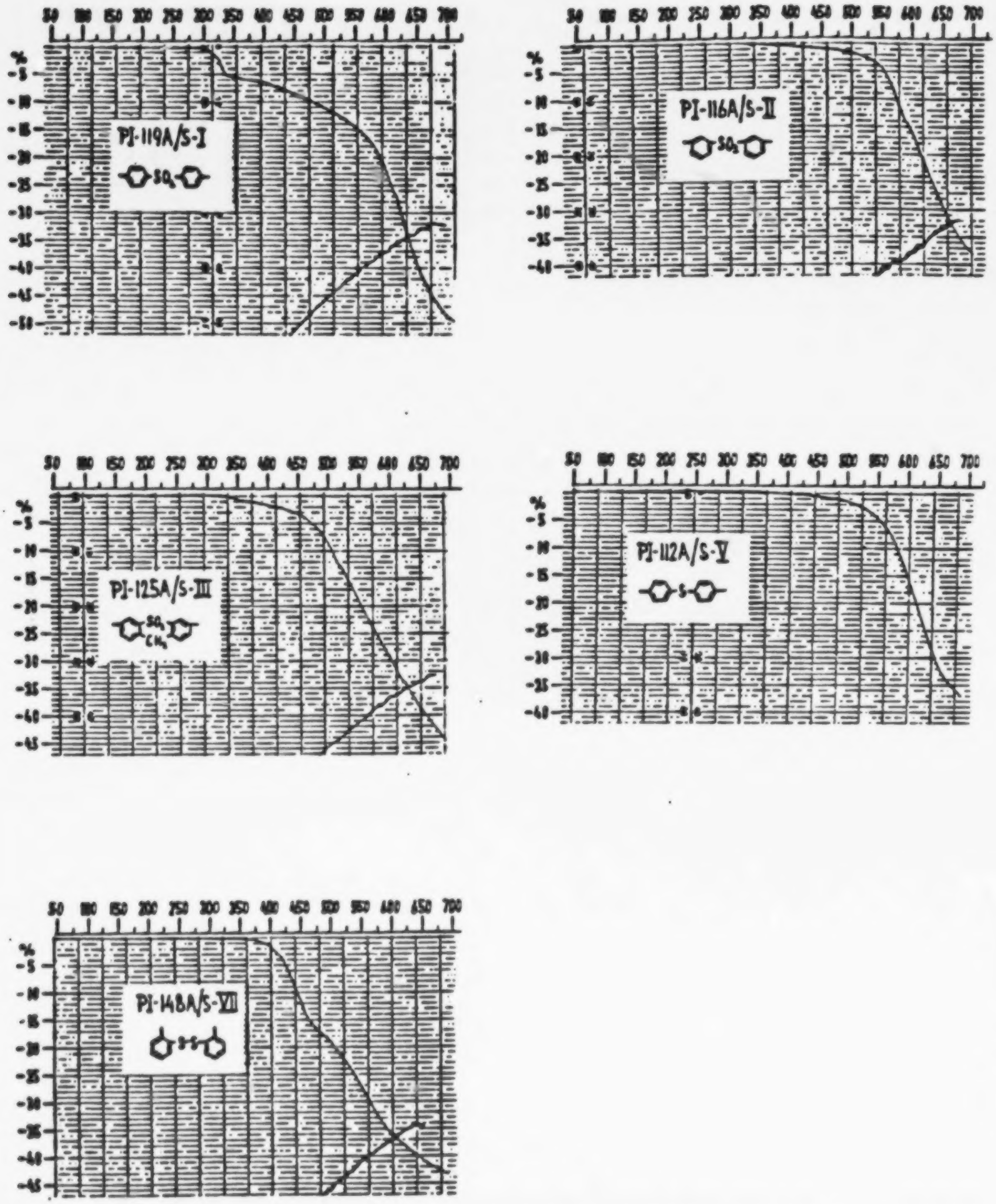


Figure 6. Thermogravimetric analysis of polyimides derived from diamines containing sulfur.

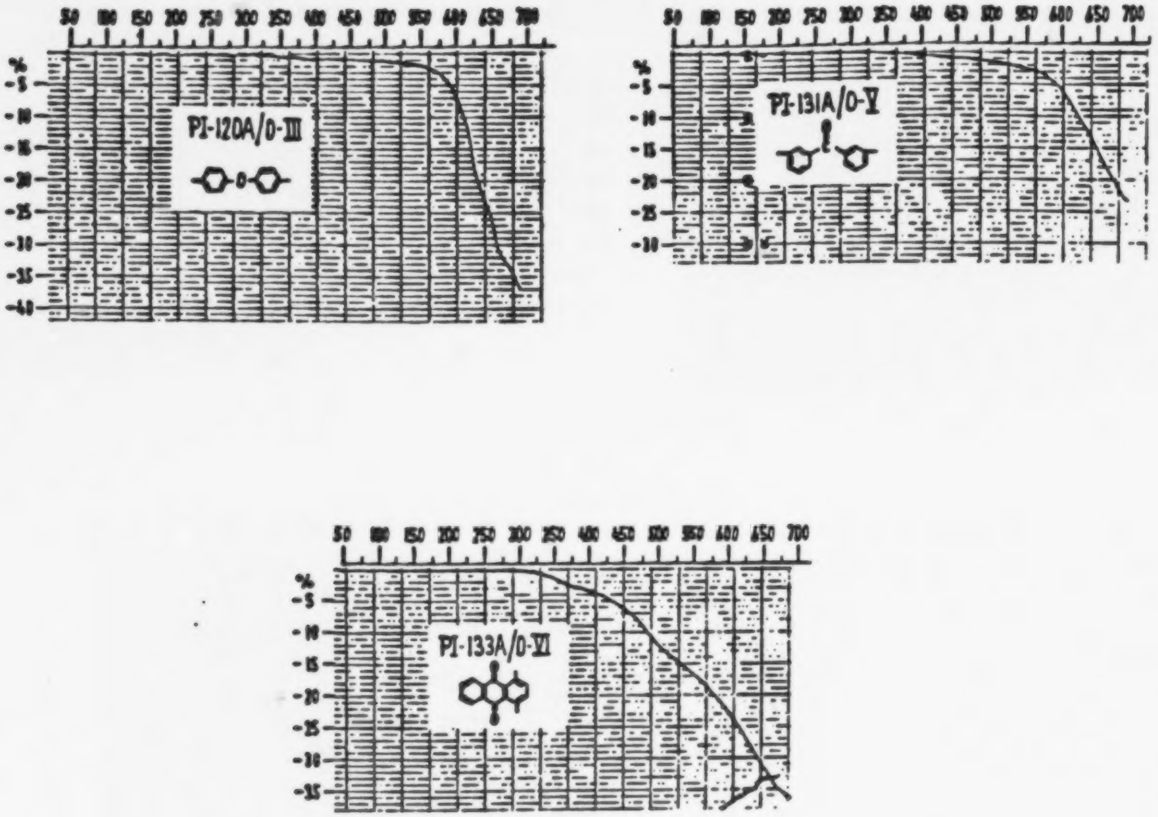
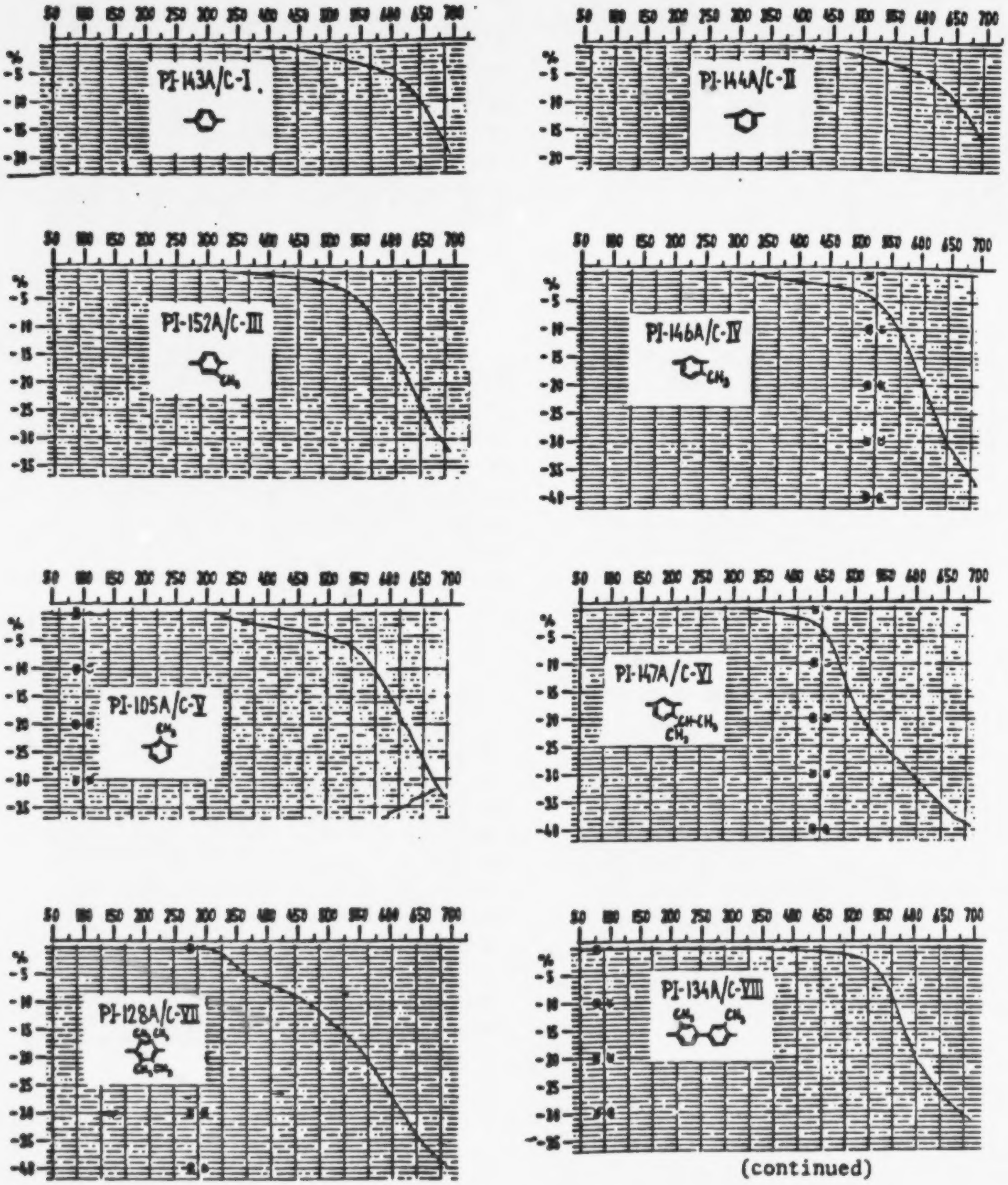


Figure 7. Thermogravimetric analysis of polyimides derived from diamines containing oxygen.



(continued)

Figure 8. Thermogravimetric analysis of polyimides derived from diamines without heteroatoms.

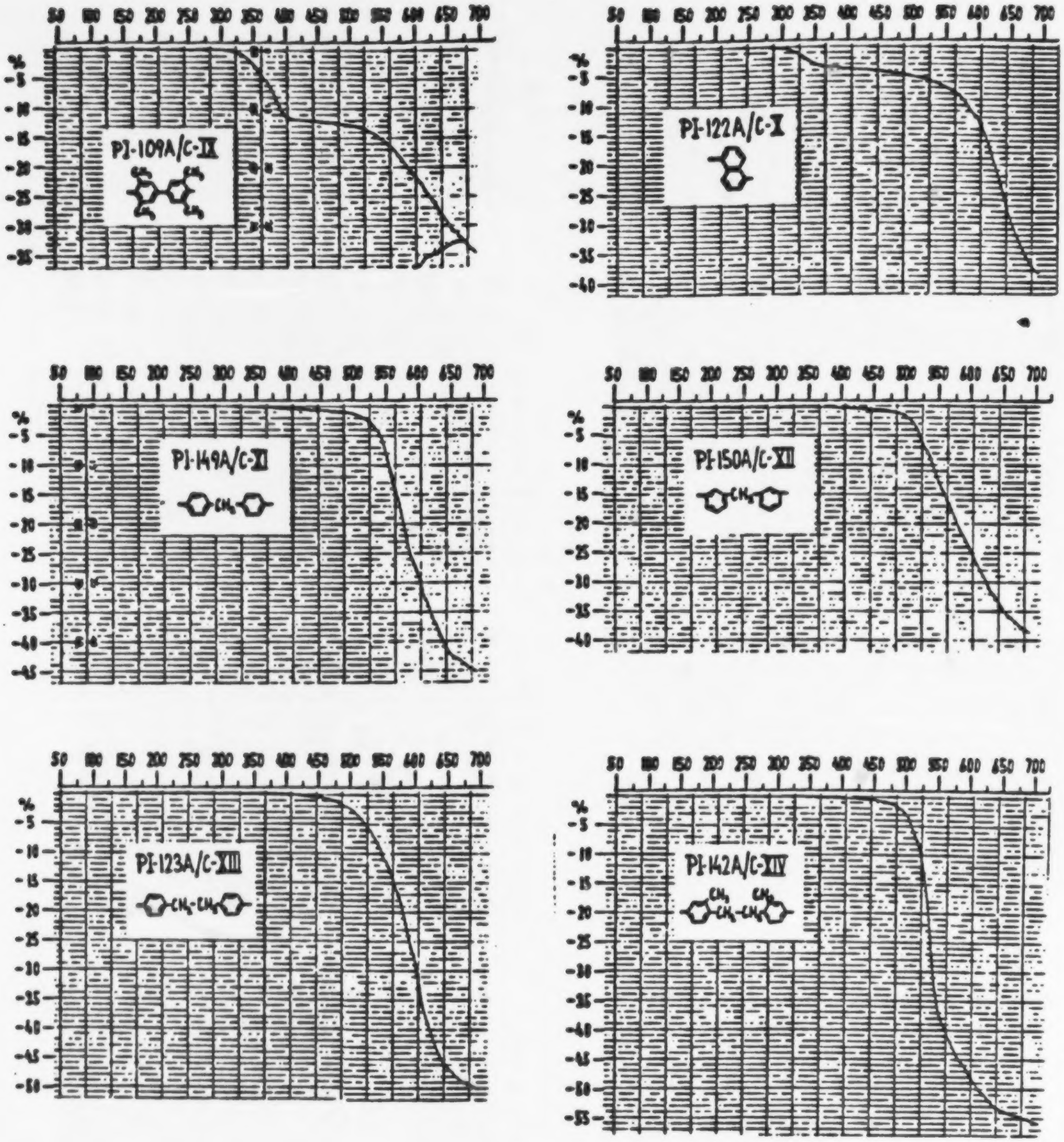


Figure 8. (continued)

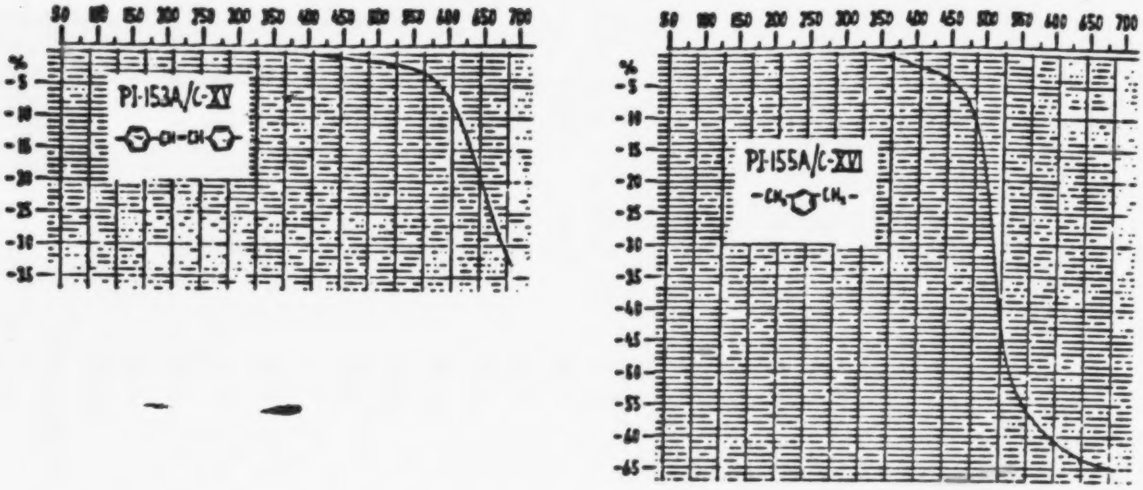


Figure 8. (continued).

Table 24. THERMOGRAVIMETRIC ANALYSIS OF POLYIMIDES DERIVED FROM PMDA AND DIFFERENT AROMATIC DIAMINES

Polyimide Number	Diamine Code	Sample Weight (mg)	1st Heating 50-300°C		2nd Heating 50-700°C			
			Onset of Wt. Loss (°C)	% Wt. Loss After 5 min. at 300°C	Onset of Wt. Loss (°C)	% Weight Loss Observed at 400°C	500°C	600°C
Polyimides from Fluorinated Diamines								
114	F-I	5.9	214	9.0	330	1.3	2.7	4.7
110	F-II	7.4	230	2.9	342	0.9	2.6	6.5
126	F-III	4.0	226	4.5	334	0.8	2.0	6.3
118	F-IV	4.5	218	14.0	338	1.0	2.3	7.0
Polyimides from Chlorinated Diamines								
103	Cℓ-I	3.9	-	9.5	310	1.5	4.0	3.9
140	Cℓ-II	6.5	238	4.2	334	2.0	6.8	14.0
121	Cℓ-III	2.9	230	10.8	278	3.5	5.0	10.5
104	Cℓ-IV	8.9	226	4.2	354	0.7	5.5	16.5
107	Cℓ-V	5.3	166	15.0	300	11.8	14.0	20.5
102	Cℓ-VI	7.7	234	4.0	254	4.0	5.5	43.0
124	Cℓ-VII	4.2	210	6.2	334	1.0	2.2	7.5
Polyimides from Nitrogen Containing Diamines								
167	N-I	7.6	-	0.1	370	0.3	2.5	20.0
111	N-II	3.9	-	9.8	326	2.2	7.5	17.0
132	N-III	4.9	-	5.0	358	1.5	6.5	21.5
129	N-V	4.2	274	2.5	322	3.3	5.5	7.3
171	N-VI	5.3	-	-	310	11.5	37.0	50.0

(continued)

Table 24. (Cont'd.)

			1st Heating 50-300°C		2nd Heating 50-700°C			
Polyimide Number	Diamine Code	Sample Weight (mg)	Onset of Wt. Loss (°C)	% Wt. Loss After 5 min. at 300°C	Onset of Wt. Loss (°C)	% Weight Loss Observed at		
						400°C	500°C	600°C
Polyimides from Sulfur Containing Diamines								
119	S-I	3.7	222	8.5	290	6.3	11.0	22.0
116	S-II	3.4	202	7.1	338	0.5	1.5	16.0
125	S-III	2.8	210	8.0	310	1.5	9.0	30.0
112	S-V	4.2	230	1.5	362	0.2	1.5	15.0
148	S-VII	3.7	238	1.8	366	1.8	19.0	36.0
Polyimides from Oxygen Containing Diamines								
120	O-III	2.5	246	2.8	290	0.8	1.2	7.0
131	O-V	8.5	210	7.0	350	0.5	1.5	6.5
133	O-VI	4.5	230	6.7	294	3.5	12.0	22.5
Polyimides from Diamines Without Heteroatoms								
143	C-I	4.1	234	2.2	390	0.1	1.8	5.0
144	C-II	3.2	234	2.7	342	0.4	1.8	5.0
152	C-III	3.6	242	2.7	334	0.5	2.1	13.5
146	C-IV	4.1	218	6.8	318	1.4	3.0	19.5
105	C-V	9.5	-	10.5	326	2.2	4.0	15.0
147	C-VI	2.8	210	3.8	326	1.4	17.0	30.5
128	C-VII	6.2	130	13.8	302	6.5	13.0	26.5
134	C-VIII	5.1	250	2.6	358	0.5	1.5	19.5

(continued)

Table 24. (Cont'd.)

Polyimide Number	Diamine Code	Sample Weight (mg)	1st Heating 50-300°C		2nd Heating 50-700°C			
			Onset of Wt. Loss (°C)	% Wt. Loss After 5 min. at 300°C	Onset of Wt. Loss (°C)	% Weight Loss Observed at 400°C	500°C	600°C
Polyimides from Diamines Without Heteroatoms (cont'd.)								
109	C-IX	7.3	242	5.0	326	11.0	13.0	21.5
122	C-X	5.4	230	8.5	294	3.8	5.0	12.0
149	C-XI	3.6	210	2.0	334	0.3	1.2	28.5
150	C-XII	7.6	254	1.2	350	0.2	1.5	24.5
123	C-XIII	9.4	274	0.3	382	0.1	2.0	29.0
142	C-XIV	3.5	258	0.6	362	0.2	3.0	47.5
153	C-XV	6.5	250	0.5	406	0	1.0	6.5
155	C-XVI	5.7	190	8.0	338	2.0	17.0	60.0

Due to similarity of chemical structure of the sorbents and the small differences in molecular weights, the "true" densities of the polymers should be quite similar. The variations in apparent densities reflect differences in porosity (directly) and specific surface area (indirectly, the specific surface area also is strongly dependent on pore size distribution).

The weight loss after conditioning was generally not higher than 10% and could be attributed to incomplete dehydration of polyamic acids in the synthesis step and desorption of the solvents used during the synthesis steps. For two polyimides (PI-102 and PI-155), the conditioning weight loss and the results of background testing (vide infra) are related to polymer decomposition.

The volatile background of conditioned sorbents was evaluated by the temperature programmed GC run. Quantitative information was extracted from the chromatogram. The inflection point in the tracing defined the maximum rate of volatilization of organic compounds from the polyimide sorbent. A tangent at this point was drawn and the $tg\alpha$ was calculated (see Fig. 9):

$$\text{Max } \mu V/\text{sec} = A/B$$

$$A = \frac{a}{\text{fsd}} \times 10^{3} \times \frac{\text{sensitivity}}{10^{-12}} \times \text{att} \qquad (\mu V)$$

$$B = \frac{b}{\text{chs}} \times 60 \qquad (\text{sec})$$

where:

a = from Fig. 9, cm,
fsd = full scale deflection of the recorder, cm,
10^3 (to convert 1 mV fsd to uV),
sensitivity = 10^{-11} amp/mV,
10^{-12} = maximum sensitivity of the electrometer, amp/mV,
att = attenuation to the recorder,
b = from Fig. 9, cm,
chs = chart speed, cm/min.

The volatile background of the polyimide sorbents is listed in Tables B1 to B6. The derived values and the temperature at which the Max uV/sec occurred (the temperature where the GC trace began to rise) are listed. The apparent retention volume of "peaks" in the GC trace and their intensity in μV at the highest sensitivity of the instrument were also recorded.

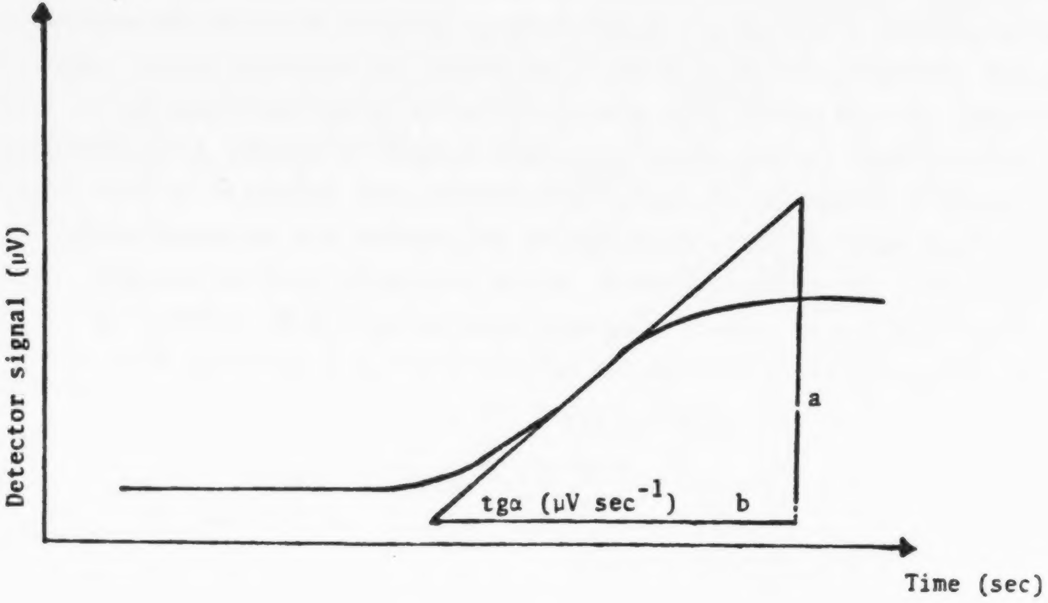

Detector signal (μV)
a
tgα (μV sec^{-1})
b
Time (sec)

Figure 9. Evaluation of the maximum value of detector signal variation.

The test described gives an overall assessment of the quantity of organic compounds evolved from the heated polyimide sorbent. In two cases, a definite decomposition of the polymeric material occurred (PI-102 and PI-155). In both cases, a >N-CH_2-bond in the polymeric backbone existed, and could be attributed to thermal instability. Differences in thermal stability between aromatic and aliphatic polyimides are well documented. The presence of the methylene group between the imide group and the aromatic group in the amine moiety precludes an extensive T_1 electron conjugation necessary for a high thermal stability of the polymer.

For the rest of the sorbents, the Max µV/sec value is comparable, and sometimes lower than the characteristic value of Tenax GC®, which is known to be a polymer with very high thermal stability.

In one case, the sorbent melted at 300°C [PI-202, a poly(benzophenonetetracarboxylic acid diimide)]. In general, the benzophenone moiety should give more flexibility to a polymeric chain, and consequently a lower melting point. When the chain includes a second flexible point, e.g., a methylene unit, the melting point is too low for the polymer to be useful.

In some cases, a very high settling of the packed columns was observed (PI-118, PI-117, PI-218). The weight loss was approximately the same as for the other sorbents; however, a change in the texture of the polymeric granules was observed.

Some sorbents in GC columns developed a very high resistance to flow (PI-115, PI-129, and PI-130). In each case, the polymeric granules were susceptible to fracturing during the packing and handling procedure. The fines formed increased the flow resistance. Increasing the mechanical stability of polymeric granules should be the objective of future work. This could be accomplished by using a crosslinking agent.

Retention Volumes, Elution Temperatures, and Number of Theoretical Plates for Test Substances in Temperature Programmed Gas Chromatography

In selecting test substances for use with temperature programmed GC, two criteria were important: (1) to scan a wide range of solute polarities and possible solute/sorbent interaction mechanisms; and (2) to employ compounds which cannot be adequately sampled by Tenax GC® sorbent.

Five test compounds are routinely used in Rohrschneider type schemes of GC stationary phase evaluation (benzene-electron donor, ethanol-hydrogen bond donor, methyl ethyl ketone-hydrogen bond acceptor, nitromethane-acidic compound, pyridine-basic compound).[3]

The alkanes C_7 to C_{10} (normal) are used to test for nonspecific adsorption.

Acetonitrile is a typical polar-neutral compound which is poorly retained by Tenax GC®.

The low molecular weight halogenated compounds also have low breakthrough volumes on Tenax GC®. Two test substances were selected from this important group, namely, 1,2-dichloroethane and vinyl chloride.

Completing the group of test substances is water, for which the lowest possible retention is desirable. Retention of water was determined in a separate experiment using isothermal conditions and thermal conductivity detection since the flame ionization detector does not detect water.

The retention of test substances was expressed in mL at room temperature:

$$V_R = t_R \times F \qquad \text{(mL)}$$

where:

t_R = retention time, min.

F = carrier gas flow rate, mL/min at room temperature.

The polymide and Tenax GC® data were compared; the retention volumes for test substances are listed in Tables C1 through C7.

The number of "theoretical plates" were calculated; however, the values obtained were not true theoretical plate values since they were generated under temperature program conditions. The concept of theoretical plates is applicable to isothermal GC. Nevertheless, an indication of the band spreading because of flow inhomogeneities and mass transfer resistance can be gleaned from such data. The calculated "theoretical plate" values were used only for comparison between sorbents tested under identical conditions.

Tables D1 through D5 present the theoretical plate data.

The elution data for the test substances are also presented as elution temperatures in Tables E1 through E6.

Selection of the sorbents for further testing (Level II) was made according to the following criteria:

- overall high retention volumes (250-500 mL/column volume employed)/ temperatures (except for water);
- low water retention (<10 mL);
- high theoretical plate values ($\geq 10^3$ range);
- large analyte capacity as expressed by constant retention volumes with increasing analyte quantity.

Additional criteria, as determined by other tests, are:

- a low volatile background (thermal stability, <0.2 μV/sec as determined by PGC);
- desirable mechanical properties of sorbent granules (e.g., particle integrity maintained under normal sampling usuage conditions).
- no significant resistance to flow when sorbent is packed in a test GC column.

The number of theoretical plates is important, because a direct relationship between collection efficiency and the number of theoretical plates for a substance has been derived, which is expressed in the simplest way by the Raymond-Guiochon relationship[4]:

$$BV = V_R(1 - \frac{2}{\sqrt{N}})$$

where:

BV = breakthrough volume, volume units;

V_R = retention volume for the sampled substance, volume units;

N = number of theoretical plates for sampled substance.

The highest number of theoretical plates attainable is desirable.

The changes in retention volumes as a function of analyte quantity provides an indication of the adsorption isotherms linearity for the test substance. If the difference is zero, or very small, for the range of sample quantity examined then the adsorption isotherm is linear. A linear adsorption isotherm for a large analyte quantity is the most desirable property.

Upon evaluating data in Tables A1-A6, B1-B6, C1-C7, D1-D5 and E1-E6, the following polyimides qualified for Level II testing:

- Chlorine-containing polyimides: PI-103, PI-108, PI-113, PI-115, PI-121, PI-124.
- Fluorine-containing polyimide: PI-126.
- Nitrogen-containing polyimides: PI-106, PI-130, PI-132.
- Oxygen-containing polyimides: no representative.

- Sulfur-containing polyimides: PI-112, PI-119.
- Polyimides from diamines without heteroatoms: PI-109, PI-149.

The number of sorbents which qualified was greater than could be handled in the Level II testing procedure. Thus, the testing plan was partially modified by beginning Level II testing with all 14 sorbents. Experiments addressing sorbent background and artifact reaction products were conducted first, and those sorbents which performed well were then further evaluated by the more labor-intensive isothermal GC retention experiments.

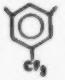
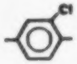
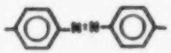
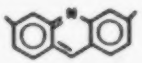
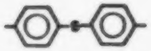
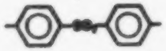
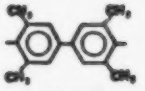
Humidity Testing on Selected Sorbents

Differences in retention volumes and theoretical plates for low *vs*. high humidity conditions are reported as percent differences in Table 25. A negative value indicates an increase in retention volume or an increase in theoretical plates under high humidity conditions.

The sorbents were ranked using retention volume and the absolute value of the percent difference for two test analytes, ethanol and vinyl chloride. Ethanol and vinyl chloride were used in the ranking procedure because they exhibit a large difference in retention volumes by virtue of the polar and nonpolar groups. Sorbents received a ranking of one if they exhibited large retention volumes with ethanol and vinyl chloride or if they had small positive or negative percent differences in retention volumes. The overall ranking of the sorbents was calculated by adding the ranking values. The smallest possible total ranking was 2, and the highest ranking was 14, as the rankings in each category are from 1 to 7. A trend between large retention volumes and small positive or negative percent differences was observed. Results are shown in Table 26.

Tenax was included in the sorbents tested under high humidity conditions. The same procedure was followed for Tenax as for the other sorbents. The mean and coefficient variation (C.V.) of the retention volumes for the test compounds were calculated with and without the presence of high humidity. The coefficient of variation was smaller when the experiment was performed under high humidity conditions indicating that high humidity had little, if any, effect on retentions on Tenax. Results are recorded in Table 27.

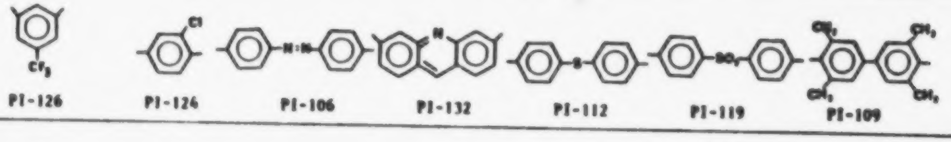
Table 25. EFFECTS OF HUMIDITY ON RETENTION VOLUMES AND THEORETICAL PLATES

	% Differences in retention volumes from humidity							
Test substances[a]	Tenax	 PI-126	 PI-124	 PI-106	 PI-132	 PI-112	 PI-119	 PI-109
Nonpolar								
Vinyl Chloride	(1)[b], 0[c]	(1), -12	(1), -12	(1), +50	(1), -41	(2), -41	(1), +72	
C7	(8), +10	(3), -1	(2), +20	0	(1), +1	(4), -1	(4), +2	
C8	(10), +9	(5), -10	(3), +8	NS	(3), +11	(9), 0	(9), -4	
C9	(11), +7	(10), -2	(5), +4	NS	(4), 0	(10), -1	(10), -3	
C10	(12), +6	NS	(9), +2	NS	(5), -2	(11), -1	NS	
Benzene	(7), +2	(7), -1	(8), -2	(4), +4	(7), -1	(8), -3	(6), +3	
Acetonitrile	(3), +4	(6), -2	(6), 0	(6), +4	(8), -6	(3), -4	(3), +7	
Dichloroethane	(6), +4	(4), -2	(7), +3	(3), +10	(11), -22	(6), -1	(5), +7	
Polar								
Ethanol	(2), +6	(2), -8	(4), -14	(2), +10	(6), +1	(2), -3	(2), +24	
Methyl Ethyl Ketone	(5), +7	(9), -3	(11), -9	(7), +12	(10), -10	(7), -3	(8), +5	
Nitromethane	(4), +11	(8), -3	(10), -1	(8), +9	(9), -4	(5), -4	(7), +6	
Pyridine	(9), +7	(11), -14	(12), -19	(9), -4	(12), -5	(12), -6	(11), -34	

The following polymers had too high a backpressure to test with humidity: 115, 130

(continued)

Table 25 (Cont'd.)



Test substances[a]	% Differences in theoretical plates from humidity							
	Tenax	PI-126	PI-124	PI-106	PI-132	PI-112	PI-119	PI-109
Nonpolar								
Vinyl Chloride	-82	-71	+70	-50	+49	+66	+98	
C7	+51	+5	+45	-37	-19	+1	-5	
C8	+51	-34	+40	NS	+50	+19	-8	
C9	+58	-164	+7	NS	+31	+1	+61	
C10	+44	NS	-15	NS	-400	-25	NS	
Benzene	-143	+39	-20	-218	+29	-87	-162	
Acetonitrile	+28	-467	-19	-110	+7	-486	-24	
Dichloroethane	-50	-174	+49	18	+81	-1	+14	
Polar								
Ethanol	-3	-7	-73	+47	+46	-5	+43	
Methyl Ethyl Ketone	+12	+3	-18	-224	-2	+22	+78	
Nitromethane	+25	0	-194	-36	+73	+12	-40	
Pyridine	+2	-905	-76	-574	-44	-12	-1,218	

The following polymers had too high a backpressure to test with humidity: 115, 130

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[a] 50 μL of each test substance was injected onto the columns.

[b] Order of elution.

[c] $\% \text{ difference} = \frac{R_H - R_H}{R_{NH}} \cdot 100$

R_{NH} = Retention volume or number of theoretical plates without humidity

R_H = Retention volume or number of theoretical plates with humidity

Table 26. RANKING[a] OF HUMIDITY TESTED POLYMERS

	Ethanol			Vinyl Chloride		
	Retention volumes	% difference	Total[b]	Retention volumes	% difference	Total
Tenax	7	(+)[c] 3	10	6	(0) 1	7
124	5	(-) 6	11	3	(+) 6	9
126	2	(-) 4	6	2	(-) 3	5
132	1	(+) 1	2	1	(+) 4	5
106	4	(+) 5	9	5	(+) 5	10
112	3	(-) 2	5	4	(+) 2	6
119	6	(+) 7	13	7	(+) 7	14

[a] Largest retention volume = 1
Least % difference = 1

[b] 2 minimum - largest retention volume and smallest % difference
14 maximum - smallest retention volume and largest % difference

[c] Positive or negative sign shows direction of change. Negative indicates an increase in retention volume with humidity.

Table 27. EFFECT ON HUMIDITY ON RETENTION VOLUMES ON TENAX

Test substance	Injection size (μL)	Low	Humidity	High	Humidity
		mean(mL)	% CV[a]	mean (mL)	% CV
C7	5[b]	270	16		
	50	270	11	260	10
C8	5	320	14		
	50	320	10	310	10
C9	5	360	12		
	50	360	9	360	9
C10	5	400	11		
	50	400	8	400	8
Benzene	5	230	5		
	50	230	7	240	7
Ethanol	5	77	3		
	50	77	12	77	11
Methyl Ethyl Ketone	5	190	9		
	50	210	13	200	12
Nitromethane	5	160	6		
	50	160	8	160	8
Pyridine	5	280	4		
	50	300	13	300	12
Acetonitrile	5	110	4		
	50	120	8	120	7
Dichloroethane	5	220	4		
	50	200	6	220	6
Vinyl chloride	1 mL	50	6	50	5

[a] $\% \text{ CV} = \frac{\text{S.D.}}{\text{mean}} \times 100$

[b] See text for levels injected.

Comparison of Retention Volumes on Tenax GC Columns

During the Level I testing, two Tenax GC® columns were prepared and tested. Comparison of retention volumes is given in Table 28, and the variation in theoretical plates for test substances is presented in Table 29.

The data also provide an overall view of the experimental variance in measuring retention volumes and theoretical plates.

Table 28. COMPARISON OF RETENTION VOLUMES ON TENAX

Test substances	Injection size (uL)	Retention volumes Mean[a]	s.d.[b]	% CV[c]	Range[d]
C7	5	269	41	15	92
	50	267	28	10	78
C8	5	320	43	13	98
	50	318	31	10	42
C9	5	365	45	12	102
	50	362	33	9	93
C10	5	404	44	11	103
	50	402	34	8	97
Benzene	5	231	11	5	25
	50	235	16	7	47
Ethanol	5	77	2	3	5
	50	77	9	11	25
Methyl Ethyl Ketone	5	195	16	8	40
	50	206	27	13	75
Nitromethane	5	161	9	5	17
	50	162	12	7	33
Pyridine	5	285	11	4	27
	50	299	39	13	105
Acetonitrile	5	114	4	4	10
	50	116	9	8	25
Dichloroethane	5	219	8	3	18
	50	202	34	6	90
Vinyl Chloride	1 mL	49	2	5	5

[a] Calculated including the retention volumes for the new Tenax column

[b] s.d. = Standard deviation

[c] $\% \text{ CV} = \frac{\text{s.d.}}{\text{mean}} \times 100$

[d] Range = highest retention volume - lowest retention volume

Table 29. VARIATION IN THEORETICAL PLATES FOR TENAX

Test substances	Injection size (µL)	Mean	s.d.	% CV
C7	5	800	757	94
	50	800	666	83
C8	5	1180	948	80
	50	1090	943	86
C9	5	1600	1124	70
	50	1730	974	56
C10	5	2110	1240	58
	50	2410	968	40
Benzene	5	700	288	32
	50	570	187	65
Ethanol	5	80	55	87
	50	160	136	64
Methyl Ethyl Ketone	5	1580	1020	46
	50	930	436	58
Nitromethane	5	790	461	56
	50	940	533	76
Pyridine	5	920	705	38
	50	1040	404	62
Acetonitrile	5	770	478	77
	50	390	301	69
Dichloroethane	5	1580	1090	69
	50	880	309	35
Vinyl Chloride	1 mL	110	44	41

SECTION 6

LEVEL II TESTING OF POLYIMIDE SORBENTS

INTRODUCTION

This chapter addresses Level II testing of polyimide sorbents. This testing procedure selects the most promising polymers for the trapping of vapor-phase organics and also generates the chemical data base linking the polymer's chemical and sorbent properties. Correlations between the polymer's chemical and sorbent properties are subsequently developed in Section 8. Also, more specific properties of the sorbent in terms of quality control aspects are addressed in this testing scheme.

The various testing procedures which were employed to develop this data base were: (a) peak asymmetry factors for selected test compounds which partially assess the collection efficiency of the sorbent for a particular solute based on theoretical plates; (b) dependence of retention volumes on analyte quantity on each of the polyimide sorbents; (c) the effect of the temperature on retention volume; (d) surface area measurement by mercury porosimetry; (e) an assessment of background which might occur from the polyimide polymer using thermal desorption high resolution gas chromatography; (f) the potential artifact products which might occur from polyimide sorbents by reaction with the reactive inorganic gases, ozone, and NO_x; and (g) the reproducibility of performance of selected polyimide sorbents for additional batches synthesized. Experiments addressing the above areas were conducted, and the results are reported in this chapter.

EXPERIMENTAL PROCEDURES

Calculation of Peak Asymmetry Factor

Three test compounds were selected for the calculation of the asymmetry of peaks that eluted from the various polyimide sorbents. The three compounds were ethanol, acetonitrile, and n-octane, representing polar and nonpolar substances. The peak asymmetry factor (PAF) was calculated as follows:

$$PAF = F \cdot 100$$

where B and F are measured at one-tenth of the peak height (Figure 10). The elution profiles for these compounds were obtained under isothermal conditions in experiments that were conducted to determine the dependence of retention volume on temperature.

Background Determination by Thermal Desorption High Resolution Gas-Chromatography

Glass cartridges (50 mm × 6 mm OD) filled with the sorbent were desorbed 4-5 h at 250°C, under helium flow, in a thermal desorption unit. Before background evaluation, sorbent cartridges were again desorbed for 2 h at 270°C, under helium flow (10 mL/min), directly in the thermal desorption unit of a Varian 3700 GC instrument. Without removing the cartridge from the thermal desorption unit, any desorbing compounds were trapped cryogenically (-190°C) in a nickel cryofocussing trap for 10 minutes, then injected by flash vaporization onto the fused silica capillary. The analysis parameters are given in Table 30.

All chromatographic analyses were performed at the same overall sensitivity setting (10^{-11} amp. mV). The integrated area was divided into two parts, for the peaks with retention times less than and greater than 15.0 min. The early-eluting peaks were hydrocarbons and traces of solvent, etc. The late-eluting peaks were, very probably, characteristic of the thermal stability of the sorbents. From the integrated area, a value was derived for comparison purposes using the relationship:

$$B = \frac{\text{Area} \times \text{Sens} \times \text{Att}}{10^{-12}} \times \frac{10^{-6}}{} \quad (10^{-6} \text{ area counts/g})$$

where:

B = "background,"

Area = integrated area for all peaks with retention times greater or less than 15.0 min, arbitrary units,

Sens = electrometer sensitivity, amp · mV,

Att = electrometer output attenuation,

g = weight of the sorbent in cartridge.

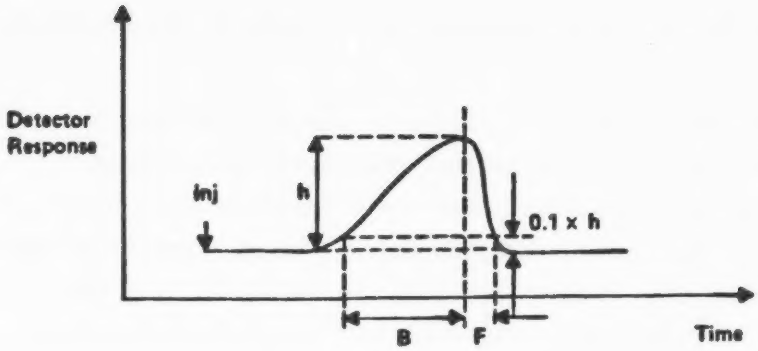

Detector Response
Inj
h
0.1 x h
B
F
Time

Figure 10. Peak asymmetry factor calculation.

Table 30. THERMAL DESORPTION HIGH RESOLUTION GAS CHROMATOGRAPHIC PARAMETERS

Parameter	Setting
Thermal Desorption Unit	
Temperature	270°C
Desorption time	10 min
He purge flow	10 mL/min
Cryofocussing trap	-190°C to 250°C in 4.5 min
Column	
Fused Silica, 50 m, wide bore (0.32 mm)	SE-54
Temperature	0 to 250°C @ 4°C/min, 250°C/10 min
He carrier flow	0.5 to 0.6 mL/min

Artifact Products from Polyimide Sorbents

The experimental system used in artifact studies is presented in Fig. 11.

Clean air ("Ultra-Zero," Matheson) after passing through a Drierite/activated charcoal trap was directed through two lines with flows regulated by a Tylan® mass-flow controller or by a fine metering valve and monitored by a Tylan® mass-flowmeter. The first line led to the ozone generator consisting of a UV lamp whose total intensity was controlled by an adjustable slide band. The second line led to two gas washing bottles, the first filled with distilled water and heated with a Brisket heating tape to 30°C. The second gas washing bottle contained glass rings (3 mm) for retaining water aerosols. The air flowing through the second line was maintained at 100% humidity; by mixing the two air flows in the appropriate ratio, any relative humidity could be achieved. A calibrated mixture of NO/nitrogen (Airco) was added at a known flowrate, using a 1° tapered fine stem metering valve and a Gilmont micro-flowmeter. The gases were mixed in a mixing chamber and passed through a reaction chamber, a sampling manifold, and then to Bendix ozone and $NO/NO_2/NO_x$ monitors.

The experimental parameters used were:

Total flow: 1 L/min air;
Ozone concentration: 200 ppb
NO_x concentration: 200 ppb (predominantly NO_2);
Humidity: 50%
Sampling time: 30 min
Sampled volume: 30 L air

The sorbent cartridges were 50 mm long/4 mm i.d. and filled with the sorbent with two glass wool plugs at each end. Before exposure to O_3/NO_x/humidity in air, the sorbent cartridges were thermally desorbed under helium flow for 2.5 h at 250-260°C.

After exposure, the cartridges were analyzed by thermal desorption high resolution GC using the parameters given in Table 30.

Comparisons were made between exposed, blank unexposed, and exposed cartridges (0 ppb O_3, 0 ppb NO_x) and between polyimide and Tenax GC® sorbents.

Again, the integrated area was divided into two parts with retention times (RT) less and greater than 15.0 min. A characteristic value for artifact products, used for comparison purposes, was derived from the relationship:

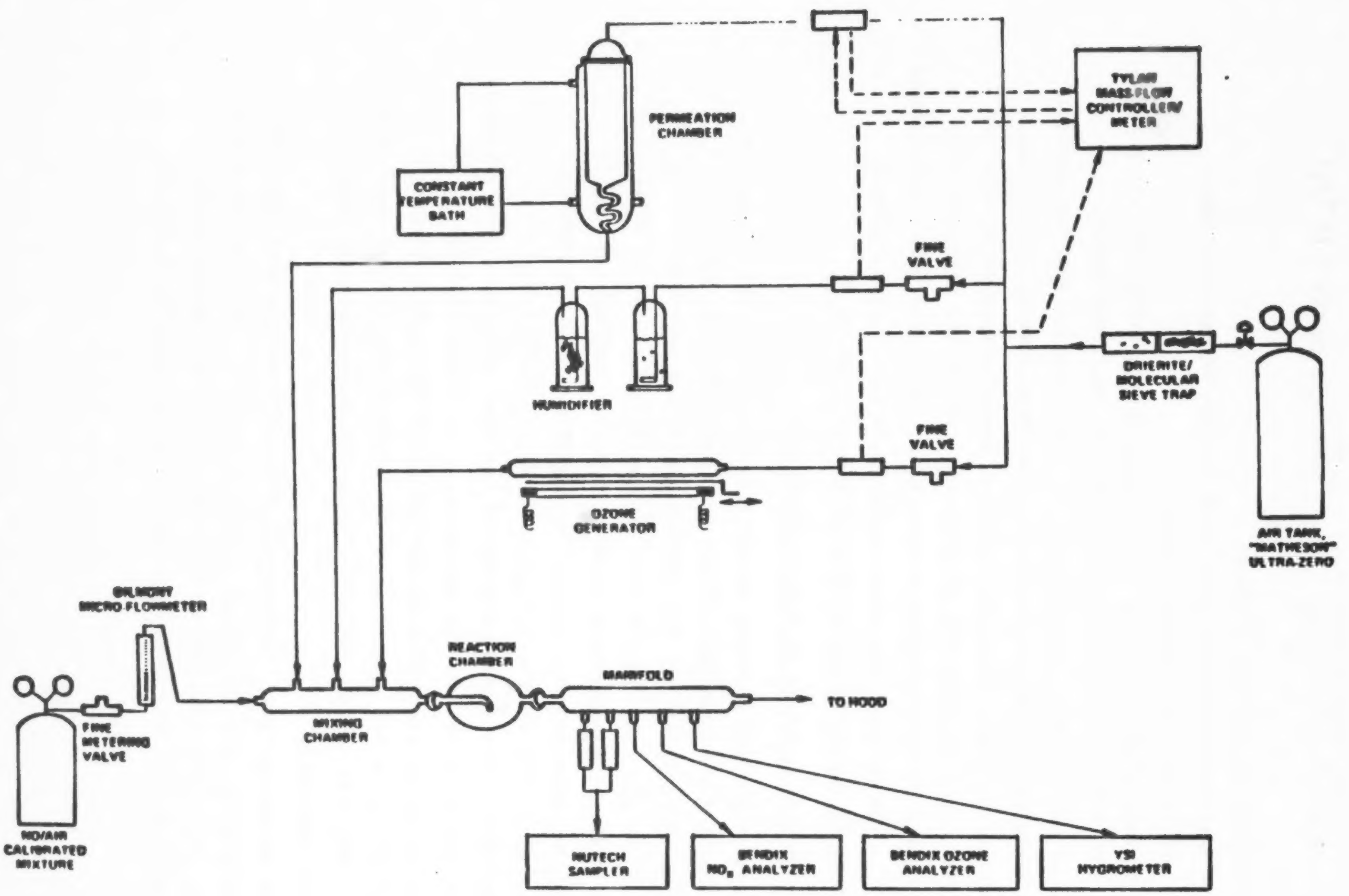

CONSTANT TEMPERATURE BATH
PERMEATION CHAMBER
TYLAN MASS FLOW CONTROLLER/ METER
FINE VALVE
HUMIDIFIER
DRIERITE/ MOLECULAR SIEVE TRAP
AIR TANK, "MATHESON" ULTRA-ZERO
FINE VALVE
OZONE GENERATOR
GILMONT MICRO FLOWMETER
NO/AIR CALIBRATED MIXTURE
FINE METERING VALVE
MIXING CHAMBER
REACTION CHAMBER
MANIFOLD
TO HOOD
NUTECH SAMPLER
BENDIX NO_x ANALYZER
BENDIX OZONE ANALYZER
YSI HYGROMETER

Figure 11. Experimental set-up for artifacts on sorbent cartridge studies.

$$A = \frac{(A_s - A_b) \times \text{Sens} \times \text{Att}}{10^{-12}} \times \frac{10^{-6}}{G} \text{ (area counts} \times 10^{-6}/\text{g)}$$

A = degree of artifact products

A_s = integrated area for peaks with RT less and greater than 15.00 min, in arbitrary units,

A_b = integrated area in the blank unexposed cartridge for all peaks with RT less/greater than 15.00 min, arbitrary units,

For some of the sorbents, the quantity of water trapped onto the sorbent was too high, leading to flow obstruction in the cryofocussing trap during TD/HRGC analysis. For these sorbents, artifact product experiments were run with 0% humidity. For the majority of sorbents, even if the cryogenic trap flow was not obstructed during thermal desorption, the "water peak" extinguished the flame during the GC run. For these sorbents, artifact products were reported only to be related to peaks with RT greater than 15.0 min.

Dependence of Retention Volume on Analyte Quantity

The effect of analyte quantity on net retention volume was studied by chromatographing different amounts of the test substances on the sorbents under isothermal GC conditions. The analyte quantities were obtained as follows. A 125 mL gas bulb wrapped with heating tape was used as a dilution chamber. The bulb was flushed with clean helium which had been passed through a coil of nickel tubing immersed in liquid nitrogen. A carefully measured aliquot of each neat test organic substance was singly injected into the heated gas bulb. Vapor-phase samples of the test substances were withdrawn from the bulb and injected onto the chromatographic column of sorbent. By using initial injection sizes of 5 μL and 100 μL of the test substance, increments of 500 ng to 100 μg or 1 mg of the analyte were chromatographed on the sorbent. The bulb was flushed with helium for 5-10 minutes between different test substances.

The same chromatographic columns used in Level I testing were employed in these experiments. The gas chromatography experiments were carried out at a temperature 30°C lower than the elution temperature determined in the Level I GC experiments. The oven temperature was continuously monitored (also checked with a thermometer permanently in place) and was ±0.2°C of the setpoint temperature. Retention time and peak widths at half height of the test substance signals were measured and the retention volumes and theoretical plates calculated.

The void volume (nonretentive volume) of the sorbent bed in the column was measured by using 100 μL of methane and measuring its transit time with a stopwatch. The inlet pressure of the columns was measured by inserting a Marsh pressure gauge through the septum of the injection port at several temperatures from 25°C to 225°C.

Determination of Temperature vs. Retention Volume Effects

The effect of variation in temperature on retention volumes was determined by injecting 500 ng to 1 μg of each test substance onto the column at three different isothermal temperatures in addition to the one chosen for the previously described concentration study. Triplicate injections of the test substances were made at each temperature.

Testing of Replicate Batches of Selected Sorbents

Samples were taken from larger replicate batches of promising sorbents and tested following the procedures listed in Section 6 on retention volumes for test substances in temperature programmed GC. Due to the number of batches to be tested and time allowed, a single 50 μL aliquot of the diluted test vapor was injected onto the sorbent.

Surface Area Measurements by Mercury Porosimetry

Surface areas were determined for polymers chosen for Level II testing by Micromeritics Inst. Corp. (Norcross, GA) and Quantachrome (Syosset, NY). Some replicate synthetic batches, blind duplicates, and recycled vs. virgin Tenax were also included for surface analysis. Mercury porosimetry was the method of choice.

RESULTS AND DISCUSSION

Peak Asymmetry Factors

Table 31 presents a comparison of the peak asymmetry for test compounds on several polyimide sorbents and Tenax GC®. It was most severe for ethanol on polyimide 119. In fact, all of the test compounds exhibited severe tailing on this sorbent. Peak asymmetry factors derived on other polyimides were comparable to that of Tenax.

Table 31. COMPARISON OF PEAK ASYMMETRY FACTORS FOR SEVERAL SORBENTS

Test Compound	Sorbent	Temperature (°C)	% PAF Mean ± S.D. (% R.S.D.)
Ethanol	119	83.4	17 ± 1.2 (6.7)
Acetonitrile	119	99.6	27 ± 1.0 (3.7)
n-Octane	119	125.4	51 ± 10.0 (19.5)
Ethanol	140	94.0	84 ± 3.2 (3.8)
Acetonitrile	140	100.4	57 ± 6.0 (10.5)
n-Octane	140	89.4	NC[a]
Ethanol	Tenax	25.4	35 ± 6.0 (17.1)
Acetonitrile	Tenax	45.8	67 ± 13.5 (20.0)
n-Octane	Tenax	94.2	67 ± 1.2 (1.7)
Ethanol	109	100.4	30 ± 4.6 (10.0)
Acetonitrile	109	120.8	69 ± 2.1 (3.0)
n-Octane	109	148.8	87 ± 2.1 (2.4)
Ethanol	149	85	59 ± 3.5 (5.9)
Acetonitrile	149	99.2	67 ± 2.9 (4.3)
n-Octane	149	130.0	36 ± 4.5[b]

[a] Not calculated, baseline instability.

[b] Average of duplicate values only.

Measurement of the peak asymmetry factor is important since it can be used as a criterion for assessing the ultimate collection efficiency of a sorbent for a particular target compound. The higher the number of theoretical plates and the more symmetrical the eluting peak from a chromatographic column, the higher will be the collection efficiency for that compound on the sorbent.

Background of the Polyimide Sorbents

The experimental results are given in Table 32. Two sorbents had a relatively high background (PI-126 and PI-147). The other polyimides are comparable with Tenax GC® with two exceptions: PI-115 and PI-124 had very low backgrounds. In fact, background was not detected at the instrument sensitivity employed for the analysis.

Artifact Products from Polyimide Sorbents

The experimental data are listed in Table 32.

In the column marked TD, the denominator lists all TD/HRGC runs with 50% humidity in the "sampled" air, the numerator lists the number of runs without problems (cryofocussing trap frozen, or FID flame extinguished).

Regarding artifact products, the polyimide sorbents can generally be divided into three groups using Tenax GC® as the reference: lower, approximately equal, and higher than Tenax GC®.

In the "lower" category, two sorbents deserve special mention. For PI-119 and PI-130, the background was very low approaching zero for early eluting peaks. The same chromatographic region for cleaned Tenax has considerable background. Again, for both, the presence of artifact products was practically zero.

Using the same classifications (low, medium, high) for thermal desorption-related problems (frozen trap, extinguished flame), a ranking of the tested sorbents was made, as presented in Table 33.

The results of Level I testing, in combination with results for background and artifact products, suggested that the following polymers should be subjected to a complete Level II testing:

PI-115 (chlorine-containing)
PI-119 (sulfur-containing)
PI-109 and PI-149 (without heteroatoms),

Complete Level II testing was performed also for Tenax GC®.

Table 32. BACKGROUND AND ARTIFACT FORMATION FOR POLYIMIDE SORBENT (LEVEL II TESTING)

Sorbent ID	Weight, mg/crt	TD, runs/runs	Background (area c x 10^{-6}/g)		Artifact (area x 10^{-6}/g)	
			RT<15	RT>15	RT<15	RT>15
PI-103(Cl)	96.5	0/3	2.6	0	-	-
PI-108	104.7	0/3	0.4	0	31	43
PI-113	153.5	2/3	0.6	0.2	8.3	0.9
PI-115	136.0	3/3	0	0	28	4.1
PI-121	94.1	-	0.03	0	very high	very high
PI-124	70.3	2/2	0	0	66	119
PI-106(N)	118.1	1/2	0.2	0.2	-[a]	0
PI-130	47.6	1/2	0	0.6	-[a]	0
PI-132	90.8	0/2	0.9	0.2	-[b]	-[b]
PI-112(S)	128.3	1/2	0.2	0.3	-[a]	91
PI-119	32.1	2/2	0	0.5	0	0
PI-126(F)	210.6	0/2	4.4	1.3	8.6[c]	4.3[c]
PI-109(C)	126.7	2/3	0.9	0.4	-[a]	0
PI-147	67.9	1/2	8.4	0	-[a]	65
PI-149	53.5	1/2	1.2	0.2	-[a]	22
Tenax GC	70.0	3/3	0.9	0.2	45	26

[a] No data, flame out at FID.

[b] Some sublimed material from the sorbent.

[c] 0% humidity.

Table 33. RANKING OF POLYIMIDE SORBENTS IN THERMAL DESORPTION/ HRGC AND ARTIFACT PRODUCT TESTING

Sorbent	Thermal Desorption	Background	Artifact Product	Number of Points (0 to 6)
PI-103	0	+	0	1
PI-108	0	+	+	2
PI-113	+	+	+	3
PI-115*	++	++	+	5
PI-121	0	++	0	2
PI-124*	++	++	0	4
PI-106	+	+	++	4
PI-130*	+	+	++	4
PI-132	0	+	0	1
PI-112	+	+	+	3
PI-119*	++	++	++	6
PI-126	0	+	0	1
PI-109*	+	+	++	4
PI-147	+	+	+	3
PI-149*	+	+	++	4
Tenax GC®	++	+	+	4

* Candidates for further Level II and possibly for Level III testing.

Dependence of Retention Volume vs. Analyte Quantity

The total retention volumes were converted to net retention volumes at the column temperature using the relationship:

$$V_n = J(t_R - t_M)F_c$$

$$F_c = F_a \cdot \frac{T_c}{T_a}\left(1 - \frac{P_w}{P_a}\right)$$

$$J = 1.5\left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right]$$

where:

V_n = net retention volume at column temperature, mL,
J = James-Martin carrier gas compressibility factor,
t_R = retention time of the solute, min,
t_M = retention time of an unretained solute (methane), min,
F_c = carrier gas flow rate in the column, mL/min,
F_a = carrier gas flow rate at ambient temperature,
T_c = column temperature, °K,
P_w = water vapor pressure at ambient temperature, kPa,
P_a = atmospheric pressure, kPa,
P_i = pressure at the column inlet, kPa,
P_o = pressure at the column outlet, kPa.

Specific retention volumes were derived using the specific surface area measurements (vide infra), from:

$$V_s = \frac{V_n}{wS}$$

where:

V_s = specific retention volume, mL/m^2,
V_n = net retention volume at column temperature, mL,
w = weight of sorbent in the analytical column, g,
S = specific surface area of the sorbent, m^2.

The number of theoretical plates for each peak was calculated from:

$$N = 5.54\,(t_R/w_{1/2})^2$$

where:

N = number of theoretical plates,

t_R = retention time, min,

$w_{\frac{1}{2}}$ = peak width at half height, min.

The test substances employed are given in Table 34.

Compared with the Level I list of test compounds, only one hydrocarbon was included in the list (additional hydrocarbons would be redundant), and two polar and volatile oxygenated compounds were added: propylene oxide and acrolein for which sampling with Tenax GC® is severely limited. Since water can not be studied at the same levels as the other test compounds because of the insensitivity of the thermal conductivity detector, it was not included in this study.

The experimental data are listed in Table F1. The data suggest that for a sample size smaller than 1.0 μg, retention is no longer quantity dependent. Within this mass range, the adsorption isotherm for each test compound can be considered, for all practical purposes, linear. This conclusion is very important, because by consistently using this sample size range, we can derive meaningful values for the thermodynamic parameters of the adsorption process, like adsorption coefficients, adsorption enthalpies, etc. from chromatographic data.

A set of graphs for sorbent PI-140 is presented in Figures 12 through 21. For less than 1 μg of test compound injected, retention data are practically independent of sample size.

Determination of Temperature vs. Retention Volume Effects

In this set of experiments, net retention volume, specific retention volume, and number of theoretical plates were calculated. The experimental data are listed in Table G1.

The number of theoretical plates decreased with decreasing temperature. Percent variation in number of theoretical plates (N) for a 10°K change in the oven temperature (T) was calculated from the relationship:

$$\frac{N_{max} - N_{min}}{N_{max}} \times 100 \times \frac{1}{T_{max} - T_{min}} \times 10$$

These data for every solute/sorbent pair are given in Table 35. For polyimide sorbents, the decrease is in the range of 10 to 20% for every 10°K change in

Table 34. TEST SUBSTANCES EMPLOYED FOR DETERMINING RETENTION VOLUME VS. ANALYTE QUANTITY

Compound	Feature
Benzene[a]	Electron donor
Methyl ethyl ketone[a]	Hydrogen bond acceptor
Ethanol[a]	Hydrogen bond donor
Nitromethane[a]	Acidic substance
Pyridine[a]	Basic substance
n-Octane	Representative hydrocarbon (in ambient air)
1,2-Dichloroethane	Low molecular weight halogenated compound
Vinyl chloride	Low molecular weight halogenated compound
Acetonitrile	Volatile polar nonionic compound
Propylene oxide	Volatile polar oxygenated compound
Acrolein	Volatile polar oxygenated compound

[a] Rohrschneider test compound.

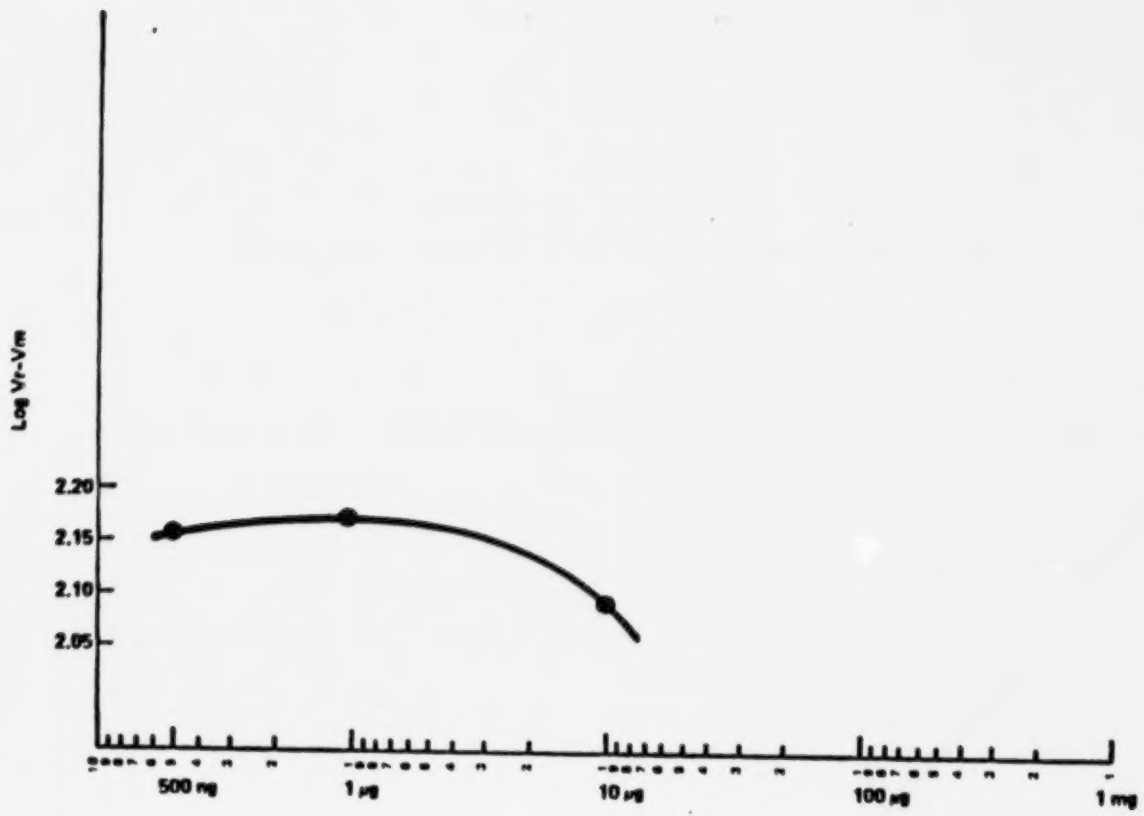


Figure 12. Log(V_R-V_m) vs. weight: n-octane on PI-140.
Temperature: 99.4°C

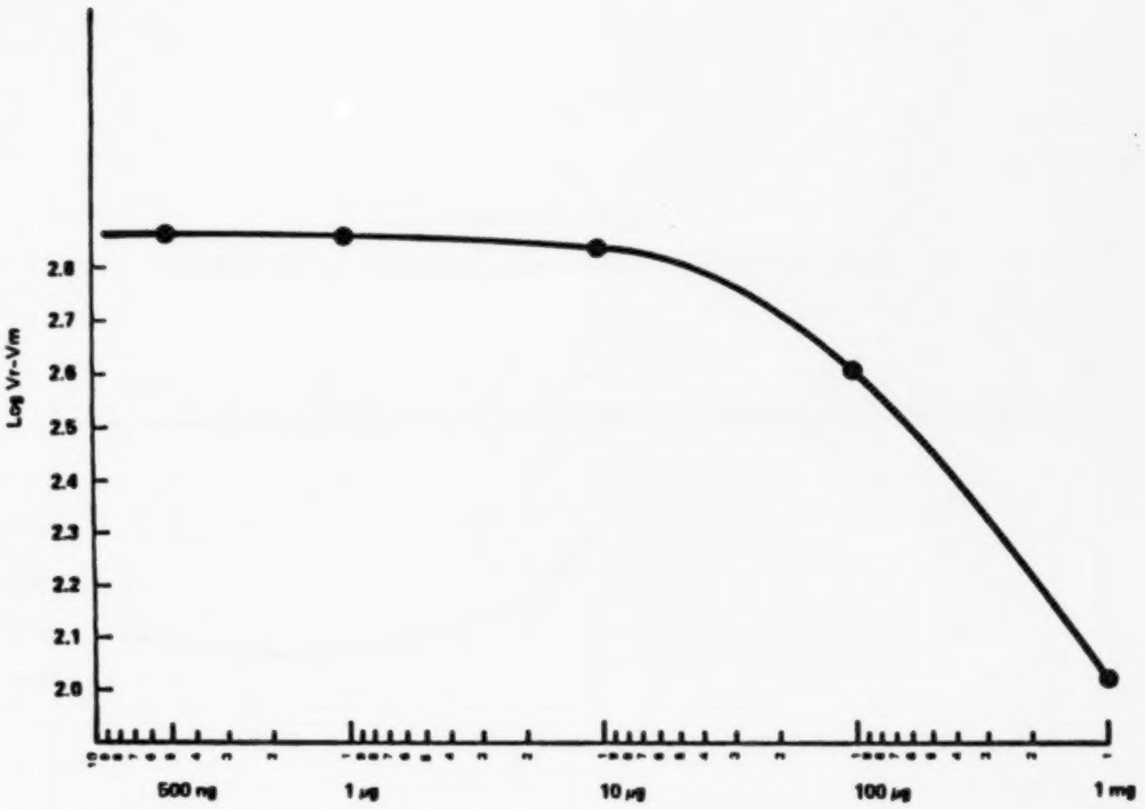


Figure 13. Log(V_R-V_m) vs. weight: benzene on PI-140.
Temperature: 119.4°C

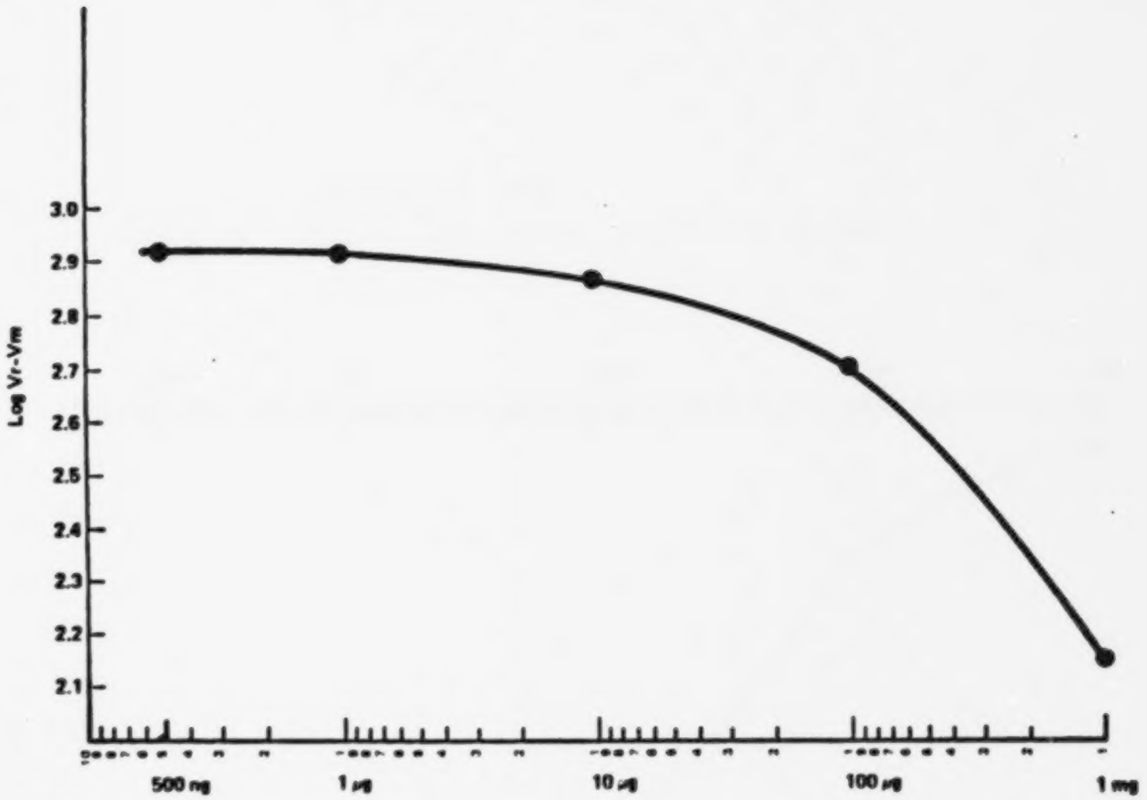


Figure 14. Log(V_R-V_m) vs. weight: methyl ethyl ketone on PI-140. Temperature: 118.8°C

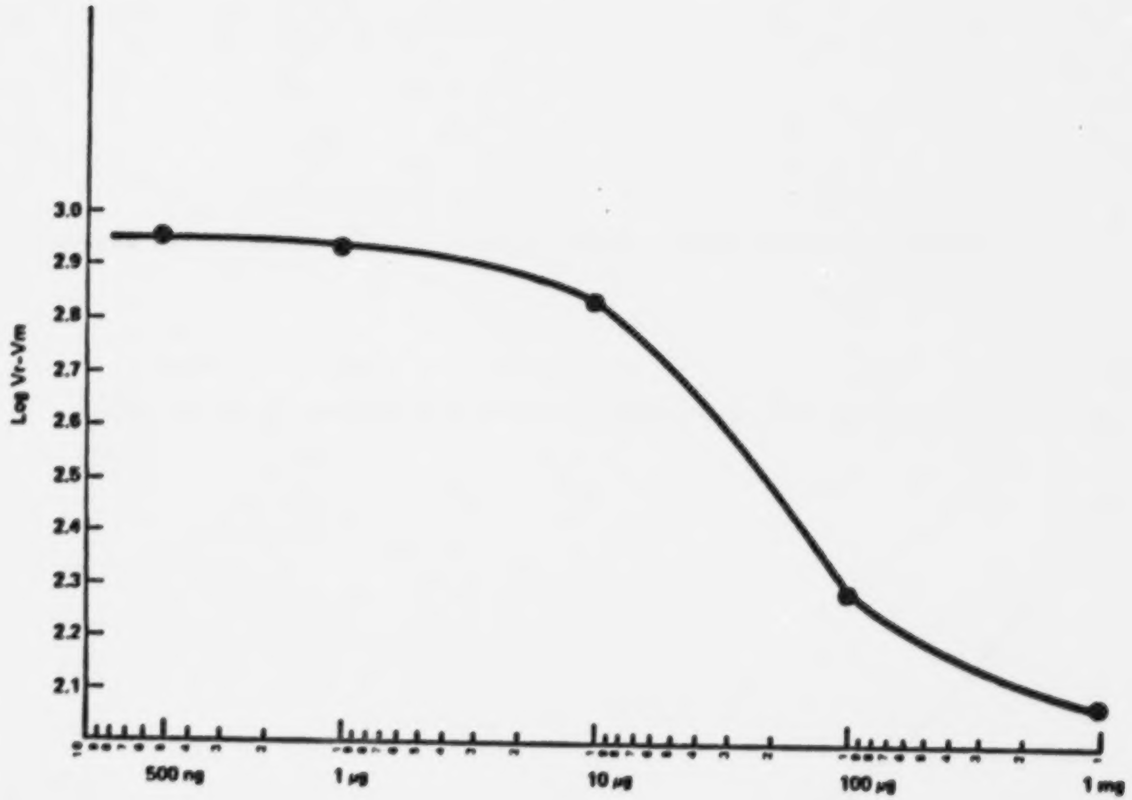


Figure 15. Log(V_R-V_m *vs.* weight: ethanol on PI-140.
Temperature: 94°C

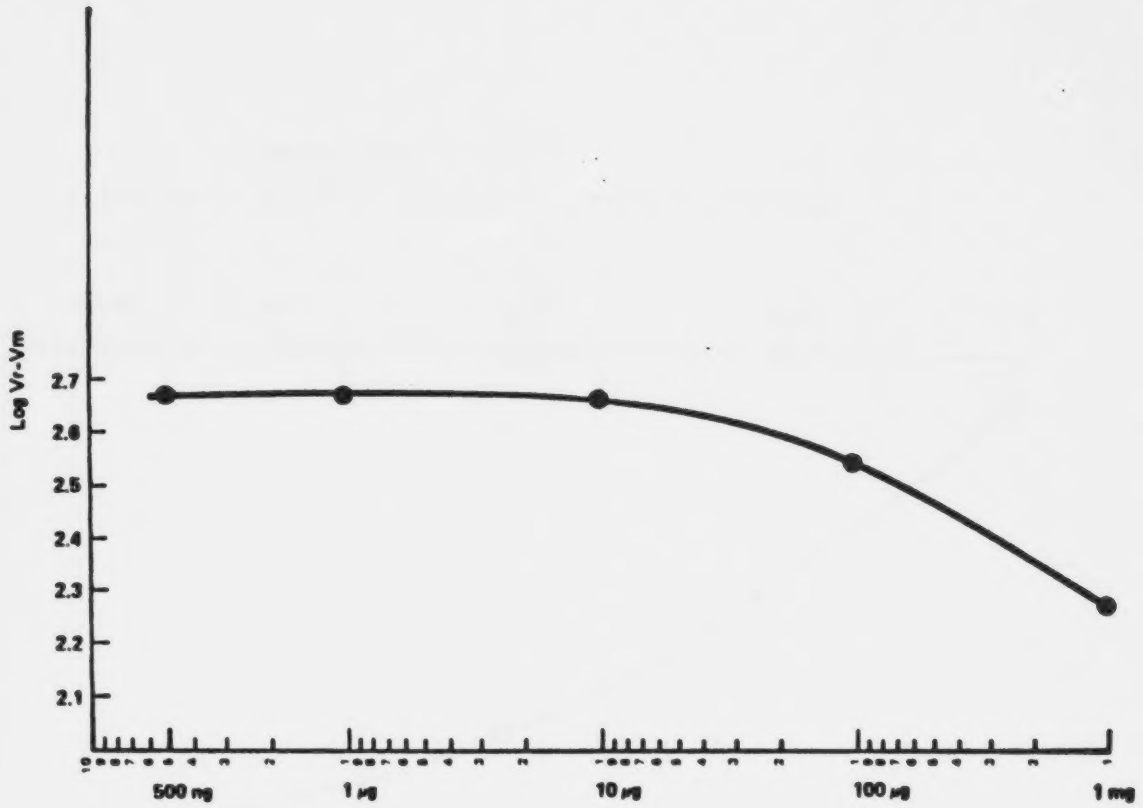


Figure 16. Log(V_R-V_m) vs. weight: nitromethane on PI-140.
Temperature: 119°C

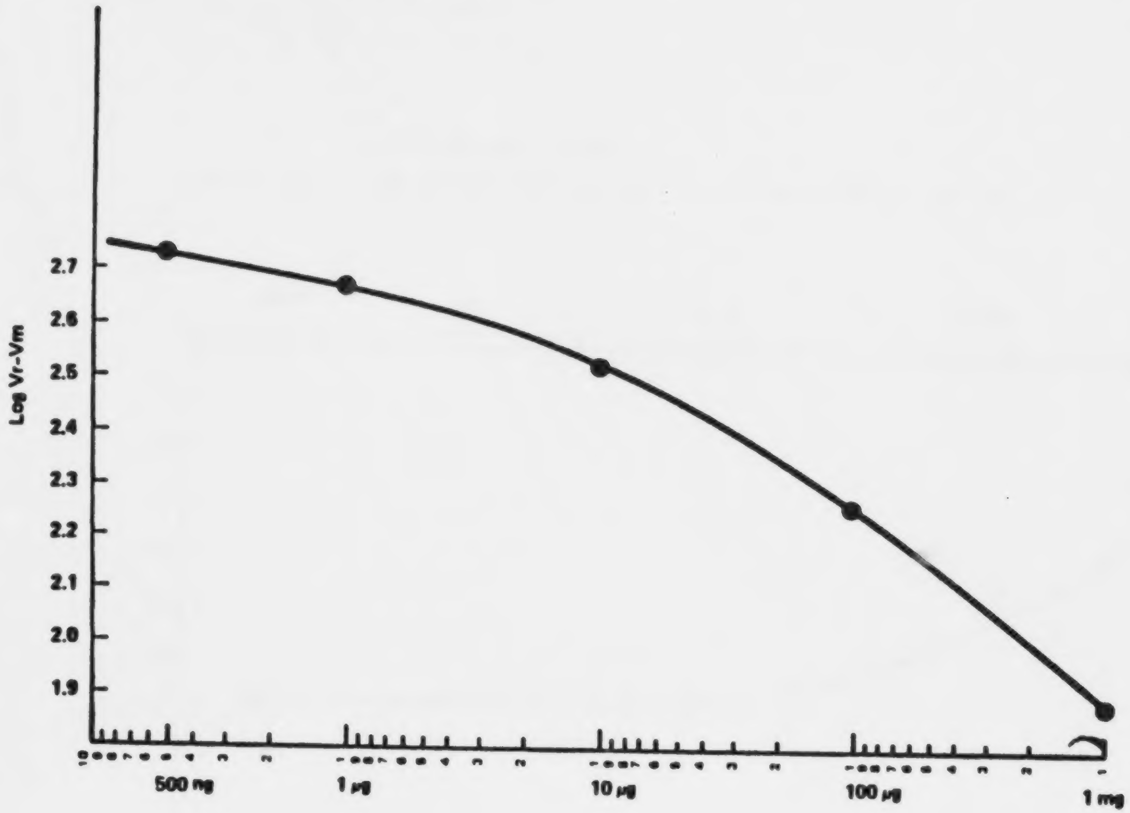


Figure 17. Log(V_R-V_m *vs.* weight: pyridine on PI-140.
Temperature: 167.4°C

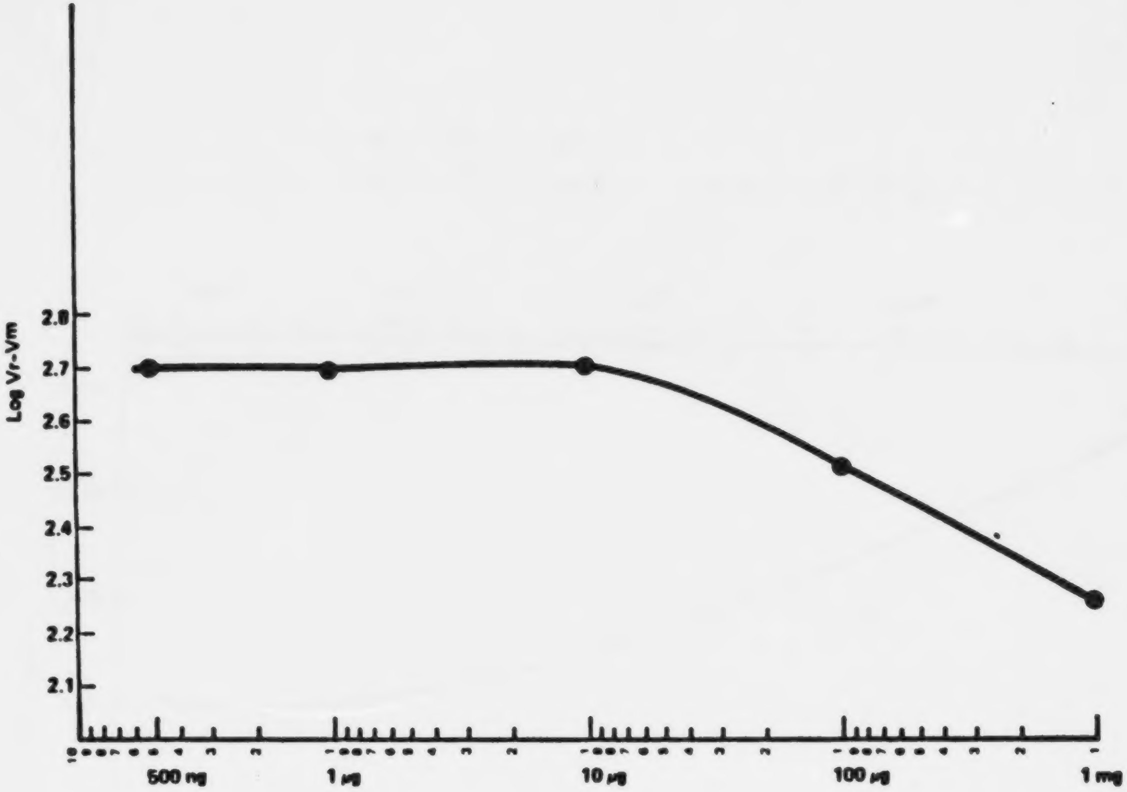


Figure 18. Log(V_R-V_m) vs. weight: 1,2-dichloroethane on PI-140.
Temperature: 117.2°C

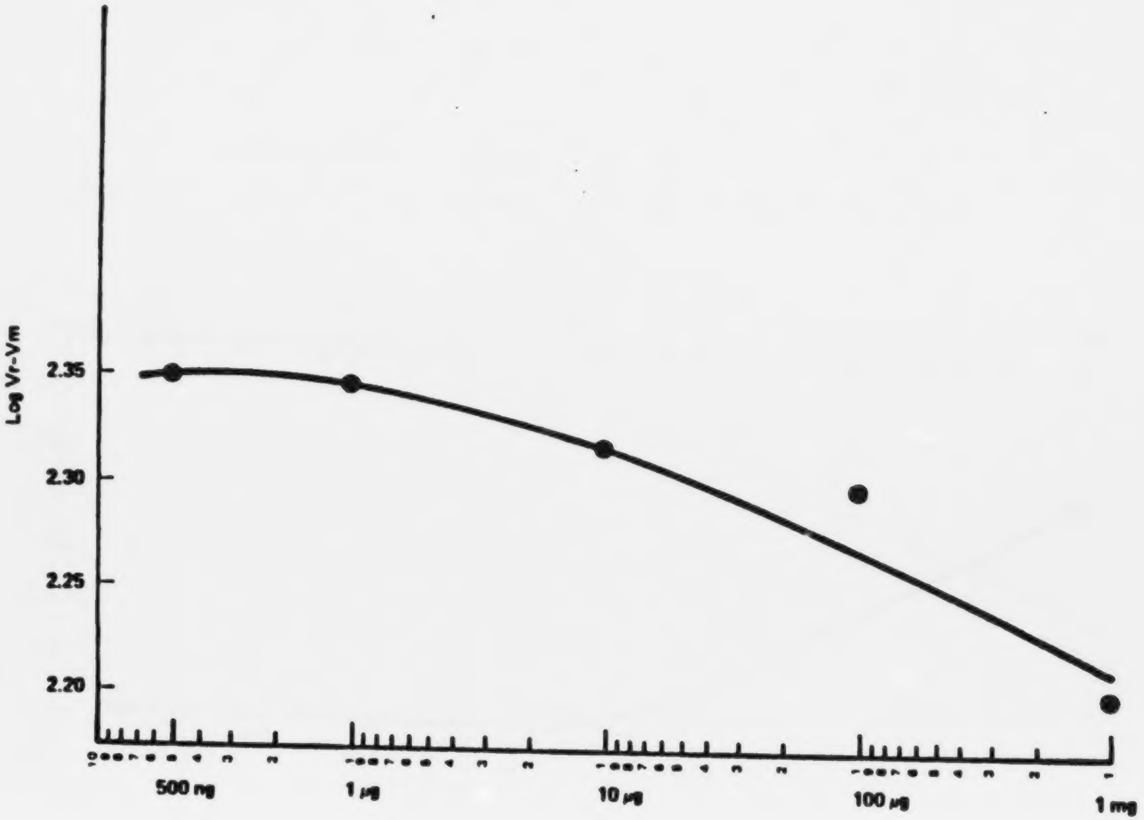


Figure 19. Log(V_R-V_m) vs. weight: acetonitrile on PI-140. Temperature: 123.4°C

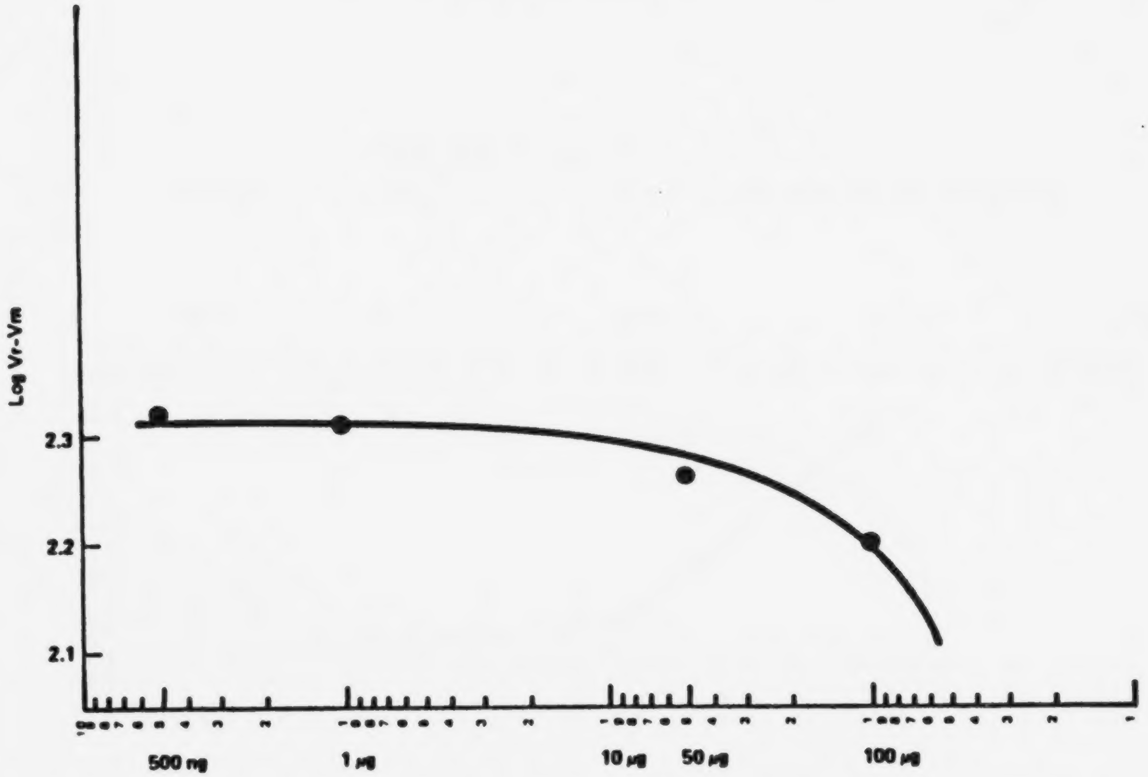


Figure 20. Log(V_R-V_m) vs. weight: acrolein on PI-140.
Temperature: 120.0°C

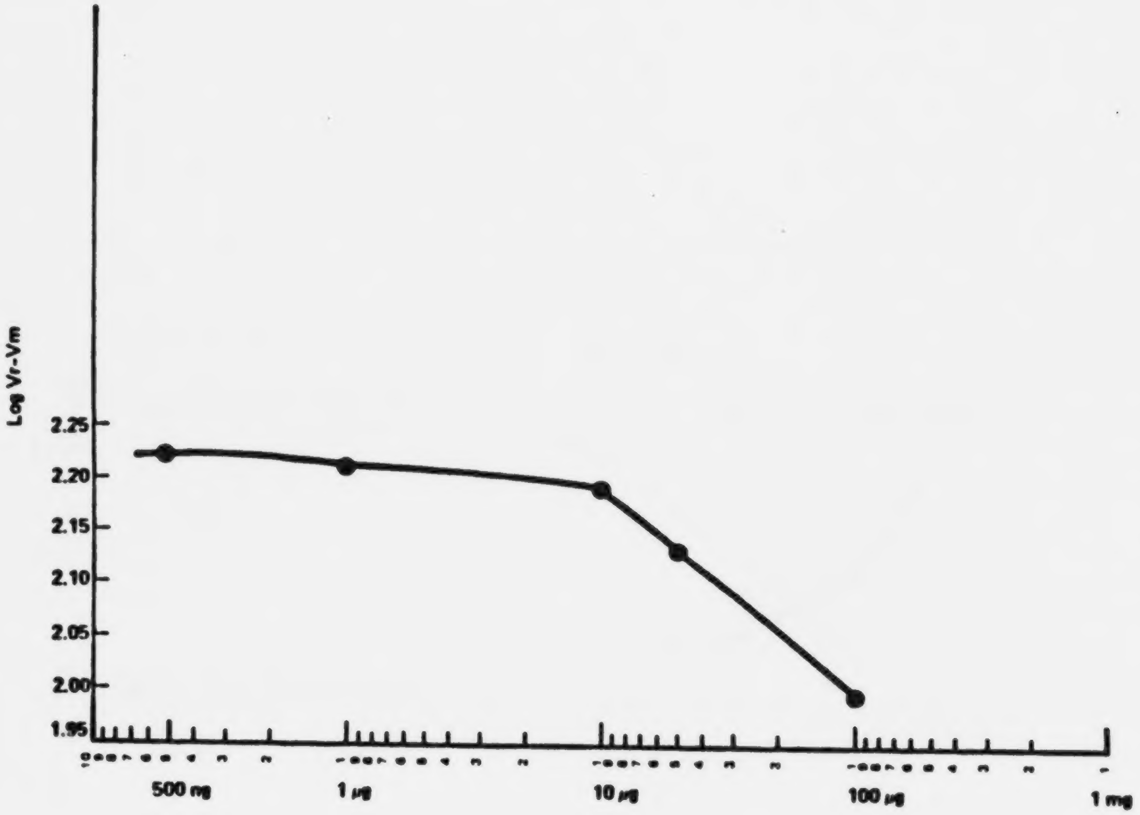


Figure 21. Log(V_R-V_m) vs. weight: propylene oxide on PI-140.
Temperature: 115°C

temperature. The dependence is nearly linear. The relatively high variability in the data and the absence of an adequate physical model prevents extrapolation to room temperature (293K) to be made. In calculations involving the number of theoretical plates, the lower experimental value was used.

In general, the number of theoretical plates for all test substances on sorbent PI-109 is very good, and the temperature dependence is significantly lower than for Tenax GC®. Sorbents PI-119 and PI-149 yield low theoretical plates for some test solutes, and PI-140(PI-115) has an order of magnitude lower plate counts for all test solutes.

The logarithm of the net retention volume dependence vs. the inverse absolute temperature is linear (Arrhenius relationship):

$$\log V_n = a + b \times \frac{1}{T}$$

The experimental points were fitted to a least squares procedure using a statistical software package (SAS, SAS Institute Inc., Cary, NC) and run on a mainframe computer (Triangle Universities Computation Center). These results are presented graphically in Figures H1 through H11 for sorbent PI-140(PI-115).

Slopes and intercepts of these regressions are listed in Table 36. As a "goodness-of-fit" parameter, the square of the correlation coefficient and the F (Fischer-Scedecor) value are also listed. The physical interpretation of R-squared is the percentage of variance in experimental data explained by the calculated relationship. The F value is the ratio between the regression sum of squares and the residual sum of squares. For a perfect linear relationship, the latter term is zero and F is infinite. By referring to F distribution tables, the confidence level for the calculated relationship can be found. For all data listed in Table 7-6, the confidence level is higher than 99.99%.

Using the linear relationships, V_n values at 20°C (293.1K) were calculated, and are listed in Table 36.

Break through volumes for 1 gram sorbent were also calculated using the Raymond-Guiochon[3] relationship:

$$BV = V_n^{20} \times \frac{1}{W} \left(1 - \frac{2}{\sqrt{N}}\right)$$

where:

BV = breakthrough volume, L/g, at 20°,

V_n = net retention volume, L, at 20°C,

Table 35. PERCENT VARIATION IN NUMBER OF THEORETICAL PLATES FOR 10°K CHANGE IN TEMPERATURE

Test compound	Sorbent Tenax GC®	PI-109	PI-119	PI-140(115)	PI-149
Acetonitrile	38	8	15	10	25
Acrolein	42	10	30	11	27
Benzene	22	13	18	16	13
1,2-Dichloroethane	22	16	12	22	14
Ethanol	37	8	22	14	19
Methyl ethyl ketone	24	14	12	13	12
Nitromethane	28	15	15	9	23
n-Octane	16	18	0	0	0
Propylene oxide	27	19	0	12	12
Pyridine	28	7	0	15	27
Vinyl chloride	35	12	18	11	19

Table 36. REGRESSION PARAMETERS FOR LOG V_n VS. 1/T WITH NET RETENTION VOLUMES EXTRAPOLATED TO 20°C

Sorbent	Compound	Slope (Logun*TK)	Intercept (Logun)	R-Square	F	UN at 20C (Liters)	BU (Liters/GM)
Tenax							
	Acetonitrile	2,550	-5.56	0.9989	9,320	1	3
	Acrolein	2,620	-5.71	0.9988	5,820	2	4
	Benzene	3,210	-6.49	0.9997	37,350	28	62
	Dichloroethane	3,170	-6.68	0.9994	17,740	20	47
	Ethanol	2,760	-6.55	0.9993	10,290	1	2
	Methyl ethyl ketone	3,230	-7.02	0.9965	3,830	17	40
	Nitromethane	2,850	-6.10	0.9988	8,560	4	10
	Octane	4,300	-8.79	0.9994	16,710	759	1,372
	Propylene oxide	2,730	-6.12	0.9984	4,421	2	4
	Pyridine	3,270	-6.27	0.9976	4,080	76	176
	Vinyl chloride	2,590	-6.38	0.9983	2,340	0	1
109							
	Acetonitrile	3,070	-5.25	0.9973	3,680	163	145
	Acrolein	3,030	-5.25	0.9992	12,850	118	105
	Benzene	3,130	-5.07	0.9993	14,060	409	360
	Dichloroethane	3,170	-5.13	0.9988	8,400	480	427
	Ethanol	3,250	-6.00	0.9987	7,810	120	104
	Methyl ethyl ketone	3,380	-5.61	0.9957	2,300	824	729
	Nitromethane	2,990	-4.84	0.9989	8,750	238	213
	Propylene oxide	3,060	-5.50	0.9983	6,410	86	75
	Pyridine	4,080	-6.37	0.9298	130	35E3	31E3

(continued)

Table 36. (continued)

Sorbent	Compound	Slope (Logun*TK)	Intercept (Logun)	R-Square	F	UN at 20C (Liters)	BU (Liters/GM)
109 (con.)							
	Vinyl chloride	2,490	-4.85	0.9997	35,100	5	4
119							
	Acetonitrile	3,250	-5.96	0.9978	4,500	134	447
	Acroelin	3,870	-7.71	0.9988	8,320	297	823
	Benzene	3,540	-6.52	0.9984	6,100	354	1,095
	Dichloroethane	3,720	-6.87	0.9986	6,470	637	2,082
	Ethanol	3,580	-7.23	0.9985	6,480	95	301
	Methyl ethyl ketone	4,180	-7.91	0.9986	7,180	2,268	7,384
	Nitromethane	3,520	-6.39	0.9993	15,320	1,357	405
	Octane	4,710	-9.14	0.9996	26,510	8,478	15E3
	Propylene oxide	3,940	-8.27	0.9934	1,510	143	426
	Vinyl chloride	3,080	-7.05	0.9943	1,750	3	10
140							
	Acetonitrile	3,300	-5.95	0.9991	11,580	203	122
	Acrolein	3,680	-7.04	0.9994	19,020	331	187
	Benzene	3,670	-6.46	0.9993	8,170	1,121	481
	Dichloroethane	3,030	-5.08	0.9882	840	187	90
	Ethanol	4,340	-8.96	0.9733	700[a]	366	366
	Methyl ethyl ketone	4,140	-7.67	0.9983	5,950	2,943	1,341
	Nitromethane	3,310	-5.75	0.9963	3,230	351	213
	Propylene oxide	3,290	-6.24	0.9984	6,210	94	42
	Vinyl chloride	2,830	-5.98	0.9976	4,200	5	2

(continued)

Table 36. (continued)

Sorbent	Compound	Slope (Logun*TK)	Intercept (Logun)	R-Square	F	UN at 20C (Liters)	BU (Liters/GM)
140 (con.)							
	Ethanol	3,389	-6.53	0.9993	8,150	107[b]	55
149							
	Acetonitrile	3,257	-6.07	0.9983	5,820	109	145
	Acrolein	3,253	-6.19	0.9990	10,040	103	80
	Benzene	3,661	-6.75	0.9984	6,280	546	482
	Dichloroethane	3,666	-6.71	0.9998	58,810	619	713
	Ethanol	3,563	-7.23	0.9998	40,120	83	100
	Methyl ethyl ketone	4,116	-7.88	0.9998	49,640	1,557	1,745
	Nitromethane	3,393	-6.15	0.9999	83,120	266	556
	Octane	4,033	-7.62	0.9948	4,340	1,369	-2E3
	Propylene oxide	3,382	-6.74	0.9999	98,410	62	64
	Pyridine	5,750	-10.56	0.9982	5,610	11E5	14E5
	Vinyl chloride	2,741	-5.96	0.9998	43,470	2	3

[a] Extrapolated value including suspect point.

[b] Extrapolated value without suspect point.

W = weight of sorbent in analytical column, g,

N = number of theoretical plates (lowest experimental value used).

The experimental data for n-octane on PI-109 and PI-140(PI-115) were highly suspect and are not listed in Table 36.

The behavior of pyridine on PI-119 and PI-140(PI-115) demonstrates considerable nonlinearity curvature. Fitting these data to a linear relationship would yield a considerable error. Data for pyridine on PI-119 and PI-140(115) were not included in Table 36.

The net retention volumes (at 20°C) for all test compounds were greater with polyimide sorbents than with Tenax GC®. For low molecular weight polar compounds, e.g., acetonitrile, the difference in retention volumes was two orders of magnitude. For less polar compounds (including octane), the differences were considerably smaller. This trend suggests that the polyimide sorbents have a considerably higher affinity through specific interactions.

The net retention volumes and the calculated breakthrough volumes were in a range which indicated that sampling for vapors of the test substances in air with any of the tested polyimides would be possible. A possible marginal case was vinyl chloride; the highest breakthrough volume (4 L/g) observed can be considered close to the practical limits if only a gram is used. Sampling for vinyl chloride in air with the polyimide sorbents, based on the listed V_n and BV values, appears to be possible but with some limitations in flow rates and sampling volumes.

In general, a comparison of all the net retention volume data reveals that the four tested polyimides are quite similar.

It is important to note that for low molecular weight, polar compounds--acetonitrile, acrolein, and propylene oxide--which cannot be sampled with Tenax GC®, high net retention volumes and breakthrough volumes can be expected with the tested polyimides.

Evaluation of Replicate Batches of Selected Sorbents

The synthesis of replicate, larger batches of polyimide sorbents should yield sorbents with the same performance characteristics. The Level I testing procedure was applied to replicate batches of four different polyimide structures [PI-115 and PI-124 (chlorine-containing), PI-109 (without heteroatom), and PI-119 (sulfur-containing)].

The general bulk characteristics of sorbents are listed in Table 37. The densities varied (coefficient of variation) from 13.9% for PI-124 to 27.0% for PI-119.

The volatile background for replicates was, in general, constant with two exceptions: a replicate of PI-124(PI-145) and a replicate of PI-119(PI-157)-- both had a considerably higher background (Table 38).

The reproducibility of retention data, as derived from temperature programmed GC experiments, was acceptable. For the sorbents PI-115, PI-124 and PI-119, the coefficient of variance for retention volumes of test substances was approximately 10% and was similar to the coefficients of variance given by testing (Level I) of two different columns of Tenax GC® at a 3 month interval (see Section 6). The retention volumes of test substances from Level I experiments are listed in Table I1 (PI-115), I3(PI-124), I4(PI-109), and I5(PI-119).

The numbers of theoretical plates are listed in Tables I2(PI-115), I4 (PI-124), I6,(PI-109) and I8(PI-119). The variance in theoretical plates was large, but again for polyimides PI-115, PI-124, and PI-119 it was similar to the variance observed for the two Tenax GC® columns.

The variance in retention data for PI-109 was considerably higher, nearly 20%. On the other hand, the number of theoretical plates was higher for all replicates in comparison with other polyimides, but their variance was considerably lower.

In general, the reproducibility for retention volume and theoretical plate data, two very important characteristics of the synthesized sorbents, was satisfactory.

Surface Area Measurements Using Mercury Intrusion Porosimetry

The surface area measurements were made by the mercury intrusion porosimetric method. The upper limit of mercury pressure was 60,000 psi which corresponds to a lower limit of intruded pores of a 30 Å radius.

The specific surface areas, pore volumes, and apparent skeletal density are listed in Table 39.

Different experimental techniques were employed by Micromeritics and Quantachrome. Micromeritics used the classical approach which consists of an incremental increase in mercury pressure and point-by-point reading of intruded

Table 37. GENERAL CHARACTERISTICS OF POLYIMIDE SORBENTS FROM REPLICATE BATCHES

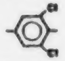
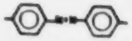
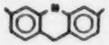
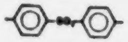
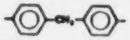
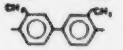
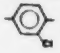
Sorbent	Weight, g (3 ft × 2 mm i.d. column)	Density g/mL	Weight loss after condit., %	Color change	General observations
PI-115	1.0215	0.426	0.6	sand-same	Very high back pressure
PI-138	1.5567	0.649	2.4	sand-same	-
PI-140	1.3795	0.575	0.6	sand-same	High electrostatic charge
PI-156	1.4967	0.624	6.2	tan-same	-
	Mean (SD, %CV): 0.569(0,100;17.6)				
PI-124	0.5925	0.247	4.2	page orange-same	Hard to pack
PI-139	0.7923	0.330	6.1	yellow-same	-
PI-145	0.6175	0.257	5.5	yellow-same	-
PI-161	0.6159	0.257	5.4	yellow-same	-
PI-162	0.5691	0.237	4.7	yellow-same	-
	Mean (SD, %CV): 0.266(0.037;13.9)				
PI-109	1.0194	0.425	4.7	tan-same	-
PI-164	0.7194	0.299	7.7	tan-same	-
PI-166	0.5941	0.248	8.2	tan-same	-
PI-170	0.7723	0.322	7.3	tan-same	-
	Mean (SD, %CV): 0.323(0.074;23.0)				
PI-119	0.2749	0.115	15.7	light yellow-same	High electrostatic charge
PI-154	0.4525	0.189	9.7	light yellow-same	-
PI-157	0.5213	0.217	8.8	light yellow-	-
PI-159	0.3522	0.147	8.2	light yellow-same	-
	Mean (SD, %CV): 0.167(0.045;27.0)				

Table 38. VOLATILE BACKGROUND OF SORBENTS FROM REPLICATE BATCHES

Sorbent	Maximum µV/sec (°C)	Plateau to °C	Peaks retention volume(mL), µV
Batches PI-115:			
PI-138	0.70(270)	218	NP[a]
PI-140	0.28(270)	250	NP
PI-156	2.28(275)	162	NP
Batches PI-124:			
PI-139	0.93(275)	194	NP
PI-145	12.13(233)	144	(490), 10,400
PI-161	5.71(229)	119	(520), 6,000
PI-162	6.95(216)	138	(600), 8,400
Batches PI-109:			
PI-164	1.68(275)	146	(750), 2,100
PI-166	4.75(258)	114	(570), 8,100
PI-170	1.45(262)	178	(580), 1,500
Batches PI-119:			
PI-157	13.1](250)	114	(520), 2,600
PI-154	1.90(256)	162	(530), 3,000
PI-159	1.93(275)	130	(780), 3,500

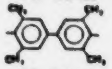
[a] NP: no peaks.

Table 39. SURFACE AREA MEASUREMENTS FROM TWO SOURCES

		Quantachrome				Micrometitics		
		Surface area (m^2/g)						
Sorbent	Similar to	Ambient to 1,200 psig	1,200 to 60,000 psig	Total	Pore volume (cc/g) 1,200-60,000 psig	Density g/cm^3	Total surface area (m^2/g)	Pore volume (cm^3/g)
	Virgin Tenax	15	54	69	2.49			
	Recycled Tenax	14	48	62	2.32			
PI-115A		6	24	30	0.80	1.58	21.1	1.65
PI-138A	PI-115A	1	27	28	0.30	1.61m	18.3	0.77
PI-140A	PI-115A	0	53	53	0.43	1.59m	40.0	0.85
PI-156A	PI-115A	3	30	33	0.37	1.66q		
PI-106A		2	36	38	0.58	1.47m	43.0	1.41
PI-132A		7	35	42	1.02	1.59m	60.6	1.87
PI-119A		20	124	144	4.89	1.25m	162.2	7.39
PI-154A	PI-119A	14	115	129	2.59	1.30q		
PI-157A	PI-119A	10	76	86	2.13	1.26q		
PI-159A	PI-119A	16	106	122	3.00	1.19q		
PI-1590	Blind of PI-159	16	75	91	3.33			
PI-1001A		2	26	28^a	0.57	1.48m	36.8	1.45
PI-1002		2	23	25^a	0.48	1.44m	38.5	1.30
PI-124A				78	1.92	1.61q, 1.47m	80.8	3.37

(continued)

Table 39 (Cont'd.)

		Quantachrome				Micromeritics		
		Surface area (m^2/g)						
Sorbent	Similar to	Ambient to 1,200 psig	1,200 to 60,000 psig	Total	Pore volume (cc/g) 1,200-60,000 psig	Density g/cm^3	Total surface area (m^2/g)	Pore volume (cm^3/g)
PI-139A	PI-124A					1.44m	20.9	2.22
PI-145A	PI-124A			61	1.85	1.55q		
PI-161A	PI-124A			68	1.88	1.54q		
PI-162A	PI-124A			64	2.03	1.75q		
PI-109A				73	0.69	1.32q		
PI-164A	PI-109A			81	1.36	1.32q		
PI-170A	PI-109A			120	1.65	1.34q		
PI-170A	PI-109A			72	1.11	1.33q		

[a] Previous Quantachrome Surface Areas - 1001-31, 1002-26.

q - From Quantachrome
m - From Micromeritics

mercury volume. Quantachrome employs a new approach that involves scanning continuously with the mercury pressure increase, and the intruded volume is also continuously recorded.

Two complete sets of graphs for PI-119 are presented in Appendix J.

SECTION 7

LEVEL III TESTING OF POLYIMIDE SORBENTS

INTRODUCTION

More detailed testing was provided under Level III. This was performed for polymers which needed to be confirmed as promising sorbents for trapping of vapors from ambient air. It also provided, through independent assessment methods, the confirmation of the physicochemical properties of the sorbent using a chromatography model. The experiments which are conducted under this Level III testing consisted of (a) the determination of breakthrough volumes by frontal chromatography, (b) the recovery of selected test compounds loaded onto sorbents using a permeation system, (c) determination of the shelf life of sorbent cartridges, and (d) electron microscopy of selected sorbents to inspect the general morphology of the surface.

EXPERIMENTAL PROCEDURES

Breakthrough Volumes by Frontal Chromatography Experiments

The experimental apparatus used for breakthrough volume determination by frontal chromatography is presented in Figure 22.

The air flow (Ultra-Zero air, less than 0.1 ppm hydrocarbons, mainly methane, Matheson) was regulated by a Tylan® mass-flow controller. A Valco six port valve was used to direct flow on/off line with the flame ionization detector and the permeation chamber. For the generation of a constant and low concentration of organic vapor in air for which the breakthrough volume on a given sorbent was to be measured, permeation tubes were used. A Haake thermostatic bath/circulator maintained the permeation chamber at 30°C. Flame ionization detectors from a Fisher-Victoreen 4400 gas-chromatograph were used to monitor the concentration of the test compound downstream of the sorbent cartidge. The output was recorded by a Varian A-25 stripchart recorder.

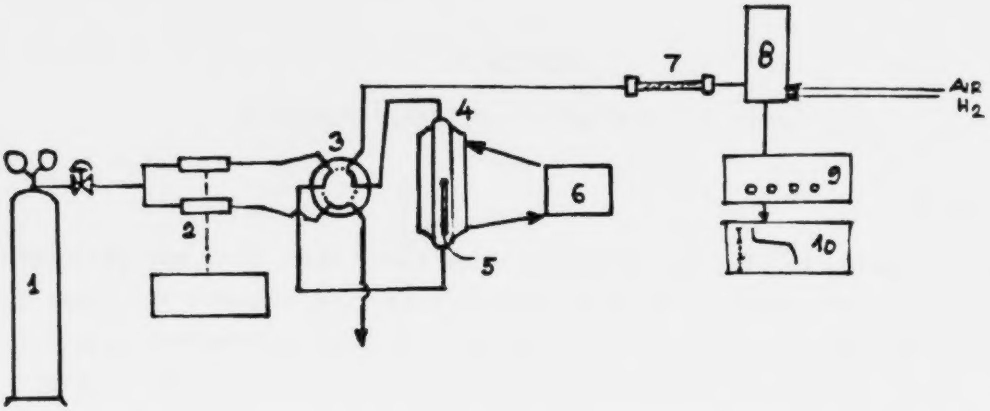


Figure 22. Experimental set-up for breakthrough volumes by frontal chromatography measurements.

1. Air tank
2. Tylan mass-flow controller
3. Valco six-port valve
4. Permeation chamber
5. Permeation tube
6. Haake thermostatic bath/circulator
7. Sorbent cartridge
8. Flame ionization detector, "Fisher-Victoreen 4400"
9. Electrometer
10. Varian A-25 strip-chart recorder

A modified version of this experimental apparatus is presented in Figure 23. Two three-port valves were used to direct flow on/off line to a gas washing bottle which was upstream from the permeation chamber. Heating tape and a variable transformer were used to control the temperature inside the gas washing bottle at 25°C. If the liquid in the gas washing bottle is pure water, a 100% relative humidity is reached in the exiting air; however, with a saturated solution of ammonium nitrate the humidity of the air is constant and equal to 63%. The humidity levels were verified with a Model 21C YSI Hygrometer.

Between the permeation chamber and the sorbent cartridge, a system for splitting flow was interposed by using a Valco zero dead volume 1.59 mm T union, two pieces of 1.59 mm o.d. stainless steel tubing of 10 to 50 cm long, and a Nupro fine metering valve (1° tapered stem). The flow through the sorbent cartridge was monitored with a Tylan flowmeter. The total flow through the permeation chamber was adjustable between 0.5 to 2 L/min, and the flow through the sorbent cartridge was 50 to 100 mL/min.

Sorbent cartridges were made from 6 mm o.d. × 4 mm i.d. glass tubing, 70 mm in length, the actual sorbent bed was 4 mm diameter x 60 mm in length (0.754 mL) and was kept secured by glass wool plugs. The sorbent weights in cartridges are listed in Table 40. After filling, the sorbent cartridges were desorbed overnight under helium flow (15 mL/min) at 270-300°C. During the last two hours of thermal desorption, the helium was purified by passing it through a liquid nitrogen bath. The sorbent cartridge was cooled under helium flow and immediately used in frontal chromatography experiments.

All experiments were conducted at 24 ± 0.5°C.

Recovery and Shelf Life of Sorbent Cartridges

Glass cartridges, 16 mm o.d. × 13 mm i.d. x 80 mm in length, were filled with sorbent, the sorbent bed was 13 mm diameter x 60 mm length (7.96 mL).

The sorbent cartridges were thermally desorbed under helium flow at 250°C. The background of sorbent cartridges was checked by thermal desorption high resolution chromatography. The experimental conditions used were given in Table 30 except that a 60 m wide bore DB-1 fused silica capillary was used.

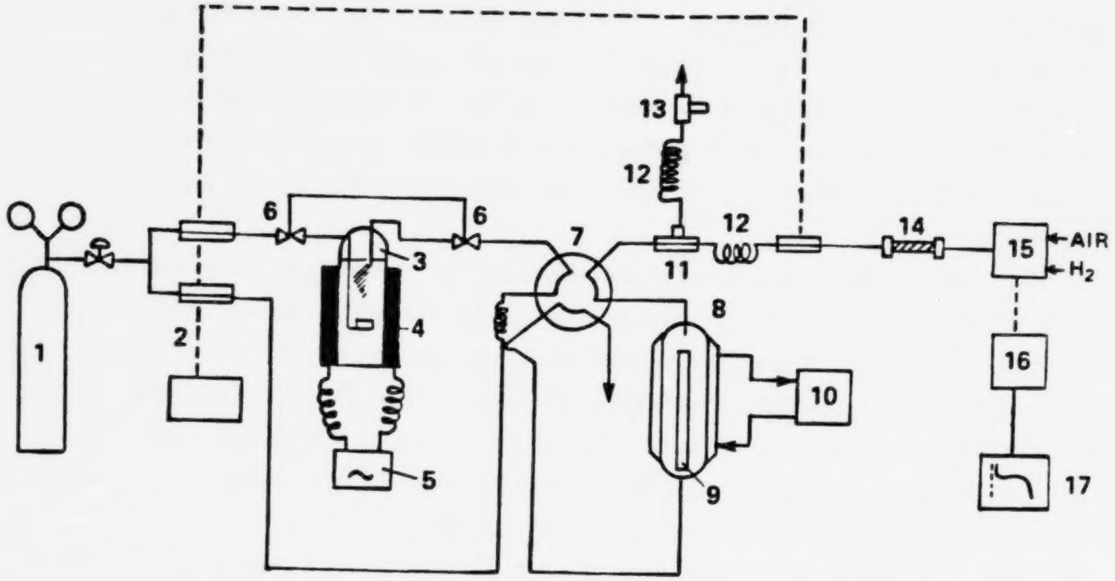


Figure 23. Modified experimental setup for breakthrough volume by frontal chromatography:

1) Air tank; 2) Tylan mass-flow meter/controller; 3) Gas washing bottle; 4) Heating tape; 5) Variable transformer; 6) Three way stopcocks; 7) Valco six-port valve; 8) Permeation chamber; 9) Permeation tube; 10) Haake thermostatic bath; 11) Valco T union; 12) SS capillary tubing; 13) Nupro fine metering valve; 14) Sorbent cartridge; 15) Flame ionization detector; 16) Electrometer; and, 17) Strip-chart recorder.

Table 40. WEIGHT OF SORBENT IN CARTRIDGES USED FOR FRONTAL CHROMATOGRAPHY EXPERIMENTS

Sorbent	Weight, mg
PI-109	274.5
	268.4
PI-119	58.0
	73.0
PI-115	370.1
	400.3
PI-149	114.4
	124.9
Tenax GC®	108.4
	109.6

4 mm i.d. x 60 mm length, 0.754 mL sorbent.

Table 41. TEST MIXTURE USED FOR RECOVERY AND SHELF LIFE OF SORBENT CARTRIDGES

Compound	BP, °C	Permeation Tube No.	Permeation Rate, ng/min	Relative Retention Time[a]
Methyl chloride	-24.2	211	464	0.43
Vinyl chloride	-13.4	2	282	0.44
Methanethiol	6.2	144	293	0.45
Propylene oxide	34.3	30	257	0.52
Methylene chloride	40	23	724	0.55
Chloroform	61.7	28	168	0.59
Acrolein	53	150	359	0.87
Methanol	65	112	436	0.92
Acrylonitrile	77.5	127	499	0.97
Benzene	80.1	19	416	1.40
2-Chloroethanol	128	153	555	1.09
		TOTAL:	4,453	

[a] Relative to perfluorobenzene, the internal standard.

The clean cartridges were loaded using a permeation system with the compounds listed in Table 41. In the permeation system, only a fraction of the carrier gas flow from the permeation chamber passed through the sampling cartridge. The loading time was set to reach a desired loading level for each compound. The total quantity loaded was equal to 4,453 ng.

Just before analysis, the sorbent cartridges were loaded with the internal standards: perfluorobenzene (PFB) and perfluorotoluene (PFT). Ten mL of internal standard vapor mixture was loaded onto the cartridge with a Precision Sampling gas-tight syringe. The vapor mixture was prepared dynamically from a permeation system. The quantities of PFB and PFT were 322 and 299 ng/cartridge, respectively.

The cartridges were analyzed by thermal desorption high resolution gas chromatography using the experimental conditions in Table 30.

The retention times of the components in the test mixtures were determined for each compound relative to PFB.

Electron Microscopy of Selected Sorbents

For the sorbents PI-109 and PI-115 and for Tenax GC®, electron micrographs were recorded using an ETEC Scanning Electron Micrograph. Sorbent samples were treated by platinum vacuum sputtering. The micrographs were recorded at a magnification of 1750.

RESULTS AND DISCUSSION

Breakthrough Volumes Determined from Frontal Chromatography

The objectives of the experiments were:

(a) To examine the agreement between breakthrough volume data from elution (extrapolation from Arrhenius plots) and frontal chromatography experiments;

(b) To determine the extent that breakthrough volumes are humidity-dependent;

(c) To determine whether breakthrough volumes are strongly dependent on competition between different compounds in a mixture; and

(d) To test the degree of adsorption of volatile organics (vinyl chloride and methylene chloride) to polyimides.

The relation between frontal and elution chromatography is depicted in Figure 24. Using identical instrumental parameters and with the adsorbent/

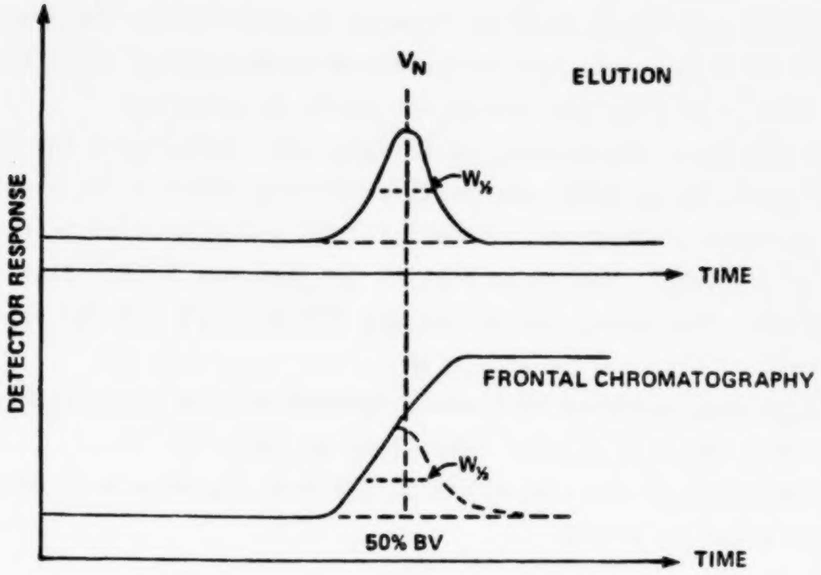

V_N
ELUTION
W½
DETECTOR RESPONSE
TIME
FRONTAL CHROMATOGRAPHY
W½
50% BV
TIME

Figure 24. Relationship between elution and frontal chromatography.

adsorbate interaction behaving as a pure physical adsorption process with a linear adsorption isotherm (ideal conditions), 50% BV and V_R should be equivalent.

The question regarding the dependence of breakthrough volumes on humidity in the sampled air remains to be answered. Contradictory data exist for Tenax GC® and for activated charcoal in the literature.[5-7]

For a pure physical adsorption mechanism at concentrations yielding linear adsorption isotherms, the retention of the components of a mixture should be independent of each other and equal to the retention of the pure compound under the same conditions of temperature, pressure, etc. The extent to which the sampling process diverges from this ideal case and exhibits nonideal behavior has practical implications for a particular sorbent. There are many unanswered questions.

Finally, the adsorption and sampling properties of the experimental polyimides for compounds like vinyl chloride, methylene chloride, and other high volatile and polar compounds are of considerable practical importance. Tenax GC® cannot be used to obtain satisfactory results for sampling of these compounds.

The 50% breakthrough time (min) was obtained directly from the recorded frontal chromatograms at the inflection point of the breakthrough curve. The 50% breakthrough volumes were calculated from the relationship:

$$50\%\ BV = 50\%\ BT \times F/V$$

where:

50% BT = 50% breakthrough time, min.

F = air flow rate, L/min

V = sorbent volume (0.75 mL)

50% BV = 50% breakthrough volume, L/mL of sorbent.

The breakthrough volume data for Tenax GC® are listed in Tables 42 and 43, for PI-119 in Tables 44 and 45, and for PI-109, PI-115, and PI-149 in Tables 46 and 47.

The air flow rate in all experiments was 50 to 100 mL/min. The flow rates were scaled proportionally down from the flow rate normally employed in actual field sampling with sorbent cartridges. For a Tenax cartridge with 13 mm diameter x 60 mm length sorbent bed, the field sampling rates are 0.5 to 1

Table 42. BREAKTHROUGH VOLUMES BY FRONTAL CHROMATOGRAPHY ON TENAX GC®: CONCENTRATION AND HUMIDITY DEPENDENCE

Compound	Concentration, ppb	50% Breakthrough time, min.	Flow Rate, mL/min	50% Breakthrough volume, L/mL^a	Difference, %^{b}
Benzene	1,700	91 116	95	11.5 14.6 13.0(3.1)	
Benzene	330	134 154	50	8.9 10.2 9.6(1.3) 11.3(2.4)^d	0^c
Propylene oxide	1,150	8	95	1.0	
Methylene chloride	2,200	12	95	1.5	
Vinyl chloride	1,200	2	95	0.25	
n-Heptane	900	265	95	33.4	
100% Humidity (24°C):					
Benzene	3,300	105	50	7.0	-38
Propylene oxide	2,200	9.5 9.5	50	0.63 0.63 0.63(0)	-37
Methylene chloride	4,150	12.6 13.0	50	0.83 0.86 0.85(0.03)	-43
n-Heptane	1,650	238	50	15.8	-53

(continued)

Table 42 (Cont'd.)

Compound	Concentration, ppb	50% Breakthrough time, min.	Flow Rate, mL/min	50% Breakthrough volume, L/mL[a]	Difference, %[b]
63% Humidity (24°C)					
Benzene	3,300	86	50	5.7	
		119		7.9	
				6.8(2.2)	-40
Propylene oxide	2,200	5.8	50	0.38	
		5.6		0.37	
		6.1		0.40	
				0.38(0.02)	-62
Methylene chloride	4,150	7.6	50	1.00	
		6.9		0.91	
				0.95(0.09)	-34
n-Heptane	1,650	194	50	12.9	-61

[a] Values from individual experiments, followed by mean (range or standard deviation).

[b] - for decrease, + for increase.

[c] Statistically not significant at 95% confidence level (Student t test).

[d] Mean (standard deviation) for all four values.

Table 43. BREAKTHROUGH VOLUMES BY FRONTAL CHROMATOGRAPHY ON TENAX GC®, CHALLENGE EXPERIMENTS

Compounds[a]	Concentration, ppb	50% Breakthrough time, min.	Flow Rate, mL/min	50% Breakthrough volume, L/mL[a]	Difference, %[b]
Propylene oxide	1,150	8	95	1.0	0
Benzene	1,700	90		11	0
Methylene chloride	2,200	13.6	95	1.7	0
Benzene	1,700	112		14	0
Benzene	1,700	92	95	12	0
n-Heptane	900	255		32	

[a] Vapor mixture.

[b] Listed as zero if less than 10% for individual experiments, or statistically not significant at 95% confidence level in a Student t test, comparing with data from Table 42.

Table 44. BREAKTHROUGH VOLUMES BY FRONTAL CHROMATOGRAPHY ON POLYIMIDE PI-119: CONCENTRATION AND HUMIDITY DEPENDENCE

Compound	Concentration, ppb	50% Breakthrough time, min.	Flow Rate, mL/min	50% Breakthrough volume, L/mL[a]	Difference, %[a]
Benzene	3,300	520	95	66	-36
	1,400	1,220	50	81	-21
	300	1,540	50	103	-
Propylene oxide	1,150	230	95	29	-24
	200	280	50	38	-
Methylene chloride	2,200	230	95	29	
Vinyl chloride	1,200	7	95	0.9	0
	900	6.7	100	0.9	-
n-Heptane	900	740	95	93	-
63% Humidity:					
Methylene chloride	4,100	2.6	50	0.34	
		4.0		0.53	
		8.3		1.1	
		5.7		0.76	
				0.68(0.32)	-98
Vinyl chloride	900	1.7	100	0.23	
		1.9		0.25	
				0.24(0.02	-73

[a] Versus the highest value.

Table 45. BREAKTHROUGH VOLUMES BY FRONTAL CHROMATOGRAPHY ON POLYIMIDE PI-119: CHALLENGE EXPERIMENTS

Compounds[a]	Concentration, ppb	50% Breakthrough time, min.	Flow Rate, mL/min	50% Breakthrough volume, L/mL	Difference, %[b]
Propylene oxide	1,150	400	95	50[c]	+33
Benzene	1,400	400		50[c]	-51
Benzene	1,700	400	95	50[c]	-51
n-Heptane	900	400		50[c]	-46
Methylene chloride	2,200	130	95	17	-41
Benzene	1,700	560		70	-32
Vinyl chloride	900	12	100	1.6	
Methylene chloride	1,500	8.7[d]		1.2	
				1.4 (0.4)[e]	+50
Vinyl chloride	900	8.6	100	1.1	
Benzene	1,650	10[d]		1.4	
				1.2 (0.24)[e]	+40

[a] Vapor mixture.

[b] - for decrease, + for increase.

[c] Single step for both compounds in the breakthrough curve.

[d] Only vinyl chloride breakthrough monitored.

[e] Mean (range).

Table 46. BREAKTHROUGH VOLUMES BY FRONTAL CHROMATOGRAPHY FOR VINYL CHLORIDE AND METHYLENE CHLORIDE ON POLYIMIDE SORBENTS

Compound/Challenge	50% Breakthrough Volumes, L/mL, mean (range)			
	PI-109	PI-115	PI-119	PI-149
Vinyl chloride/-	3.2(1.3)	1.5(0.2)	0.9(0)	1.4(0.05)
Vinyl chloride/ methylene chloride	3.2(0.4)	1.3(0.14)	1.4(0.4)	1.4(0.06)
Vinyl chloride/benzene	4.0(0.7)	1.4(0.11)	1.3(0.24)	1.5(0.24)
Vinyl chloride/humidity	1.3(0.12)	0.40(0.11)	0.24(0.02)	0.3(0)
Methylene chloride/-	26	11	29	13
Methylene chloride/ humidity	3.0(0.2)	2.0(0.02)	0.68(0.32)	2.0(0)

Concentrations:
Vinyl chloride - 872 ppb; Methylene chloride 2,068 ppb; Benzene 1,652 ppb.
Humidity: 63% rel. at 24°C.
Flow rate: 100 mL/min.

Table 47. BREAKTHROUGH VOLUMES BY FRONTAL CHROMATOGRAPHY: CHALLENGE EXPERIMENTS ON POLYIMIDE SORBENTS, STATISTICAL ANALYSIS OF DATA

Compound/Challenge	% Difference[a]			
	PI-109	PI-115	PI-119	PI-149
Vinyl chloride/ methylene chloride	0	0	0	0
Vinyl chloride/ benzene	0	0	0	0
Vinyl chloride/ humidity	-60	-73	-73	-77
Methylene chloride/ humidity	-89	-82	-98	-85

[a] - for decrease; zero for differences not statistically significant at 90% confidence level in a Student t test.

L/min. The ratio of the square of the diameters of the sampling cartridge to the sorbent cartridge used in the breakthrough experiments is:

$$13^2/4^2 = 10.56$$

Thus, the scaling down ratio for the air flow rate should be approximately 10 in order to maintain an identical linear velocity (cm/sec) between the BV experiments and air sampling. In the range investigated, the 50% BV was essentially independent of flow rate.

For Tenax GC®, the breakthrough volumes for each test compound were virtually independent of the concentration of test compounds in the range investigated (300 to 1700 ppb). The difference between the 50% BV at 330 and 1700 ppb benzene was statistically not significant (Student t test, 95% confidence level). It follows that the benzene adsorption isotherm was, in this concentration range, essentially linear. Benzene was the second most retained compound of the test compounds used and for the compounds less retained - propylene oxide, methylene chloride and vinyl chloride at a similar concentration - the adsorption isotherm should also be essentially linear.

For PI-119, the 50% BV increased with decreasing concentration of test compounds (benzene and propylene oxide, Table 44). The adsorption isotherm for the test compounds in the concentration range investigated was nonlinear.

The breakthrough volumes derived from frontal and elution chromatography were compared for the same pair of test compounds and sorbents (isothermal gas chromatography experiments, Section 6). Using the Arrhenius relationship:

$$\log V_N = a \times \frac{1}{T} + b$$

the net retention volumes at 24°C were calculated and divided by 2.4 mL, the sorbent volume in the column used in isothermal GC experiments. These values, together with 50% BV's, are listed in Table 48. The agreement was poor for Tenax GC® and acceptable for polyimides, except PI-109.

The overall acceptable agreement between data generated by the two different experiments underscores the legitimacy of both methods for generating breakthrough volume data.

The humidity dependence of breakthrough volumes was clearly demonstrated by the data listed in Tables 42, 44, and 46. There was essentially no difference between 63% and 100% relative humidity on Tenax GC®. For all tested compounds, the breakthrough volumes were significantly reduced by 35-60%

Table 48. COMPARISON OF BREAKTHROUGH VOLUMES DERIVED FROM ELUTION AND FRONTAL CHROMATOGRAPHY

Sorbent	Compound	V_N(24°C), L	V_N/2.4, L/mL	50% BV, L/mL
Tenax GC	Benzene	20	8.5	11
	Propylene oxide	1.2	0.50	1.0
	Vinyl chloride	0.21	0.09	0.25
PI-119	Benzene	250	100	100
	Propylene oxide	96	40	38
	Vinyl chloride	2.1	0.87	0.90
PI-109	Vinyl chloride	3.5	1.5	3.2
PI-115	Vinyl chloride	3.6	1.5	1.5
PI-149	Vinyl chloride	3.5	1.5	1.4

humidity. For the polyimide sorbents, the humidity effect is more dramatic. For PI-119, the humidity reduced the breakthrough volume of methylene chloride by more than one order of magnitude. A less pronounced, but still significant affect on the other polyimides was observed. Nonetheless, even with humidity reducing its breakthrough volumes, PI-109 still has practical value for field sampling.

The results of additional challenge experiments are listed in Tables 43 (Tenax GC®), 45 (PI-119), and 47 (other polyimides). On Tenax GC®, for all mixed pairs investigated, there was no difference in the breakthrough volume between mixtures and pure test compounds. Tenax GC® is probably behaving like an "ideal" physical adsorption sorbent.

In contrast, PI-119 (Table 45) depicts a different relationship. For propylene oxide/benzene, benzene/n-heptane and methylene chloride/benzene pairs, there was a decrease in breakthrough volumes. An isotonic step for both compounds in the breakthrough curve was observed. (The significance of the increase in the BV for propylene oxide in Table 45 is questionable).

An apparent increase in the breakthrough volumes of vinyl chloride on all polyimides was observed when challenged with methylene chloride and benzene. Statistical analysis of the data (Table 47) indicates, however, that the differences were not significant at 90% confidence level. Even though the increase was not statistically significant, the observation that the breakthrough volumes of vinyl chloride were not decreased is remarkable and suggests a different mechanism of adsorption is operative.

Using the 50% BV data, sampling volumes for a cartridge (standard dimensions of 13 mm diameter x 60 mm in length sorbent bed) can be calculated using the Raymond-Guiochon relationship:

$$SV = 50\%\ BV \times V \left(1 - \frac{2}{\sqrt{N}}\right)$$

where:

SV = sampling volume, L;

50% BV = 50% breakthrough volume, L/mL;

V = sorbent bed volume, mL (7.96 mL);

N = number of theoretical plates.

The number of theoretical plates, N, was calculated for a compound/sorbent pair from the experimental breakthrough curves. The geometric construction necessary for deriving an equivalent "half width" was presented in Figure 24. Thus, the number of theoretical plates was calculated from the relationship:

$$N = 5.54(50\%\ BV/"w_{1/2}")^2$$

The calculated sampling volumes are listed in Table 49 for Tenax GC®, Table 50 for PI-119, and Table 51 for the other polyimides. It is very important that the SV values of PI-109 are in the practical range for the tested compounds (vinyl chloride and methylene chloride), regardless of challenge by other compounds or humidity.

Recovery and Shelf Life of Sorbent Cartridges

The three most promising polyimides with respect to adsorption properties were included in this study. Tenax GC® was also included for comparison.

The background of sorbent cartridges (7.96 mL sorbent, 13 mm diameter x 60 mm sorbent length) was determined immediately after thermal conditioning and with time. The experimental results are presented in Table 52.

Polyimide PI-119 had a high initial background, even after 56 hours of thermal conditioning. For this polyimide, a synthesis with highly purified starting materials must be considered.

The PI-109 sorbent had a high background after 8 hours of thermal conditioning which is comparable to PI-119. With a 56 h thermal conditioning period, the background went down substantially. After two weeks of storage, background was again too high. A resynthesis of PI-109 starting with highly purified materials should be considered. The background of polyimide PI-115 was acceptable and relatively stable over time. It should be noted that in the synthesis of this sorbent, a purified diamine was used.

The results of thermal desorption high resolution gas chromatographic analysis of loaded and stored cartridges are presented in Tables 53 (Tenax GC®), 54 (PI-109), and 55 (PI-115).

In the chromatograms derived from Tenax GC® cartridges, only three of the eleven compounds in the test mixture--methylene chloride, chloroform, and benzene--were unequivocally identified by retention times. The early eluting peaks were small and buried in a relatively high background.

Table 49. SAMPLING VOLUMES AT 24°C: TENAX GC[a]

Compound(challenge)	50% BV, L	N[b]	SV, L[c]
Benzene (-)	90	41(10)	62
Benzene(Propylene oxide)	90	34	59
Benzene(Methylene chloride)	110	49	80
Benzene(n-Heptane)	92	61	69
			68(9)
Propylene oxide(-)	8.0	50	5.7
Propylene oxide(Benzene)	8.0	64	6.0
			5.9(0.3)
Vinyl chloride(-)	2.0	88	1.6
Benzene (63% rel. humidity)	54.2	93(9)	43
Benzene (100% rel. humidity)	56	67(3)	42
			43(1)
Propylene oxide (63% rel. humidity)	3.0	37(3)	2.0
Propylene oxide (100% rel. humidity)	5.0	45(0)	3.5
			2.8(1.5)

[a] Sampling cartridge: 13 mm i.d. × 60 mm in length sorbent bed, 7.96 mL sorbent.

[b] Number of theoretical plates for 60 mm sorbent bed, air at 24°C, and linear velocity 13.3 cm/sec.

[c] Sampling volume from Raymond-Guiochon relationship. In parentheses, standard deviation or range (for duplicate experiments).

Table 50. SAMPLING VOLUMES AT 24°C: POLYIMIDE PI-119[a]

Compound (challenge or concentration, ppb)	50% BV, L	N[b]	SV, L[c]
Benzene (3,000)	550	115	424
Benzene (1,300)	640	175	547
Benzene (300)	820	264	719
Benzene(Propylene oxide)	400	55	293
Benzene(n-Heptane)	400	60	298
Benzene(Methylene chloride)	560	221	482
			460(160)
Propylene oxide (1,150)	230	29	145
Propylene oxide (220)	300	33	197
Propylene oxide(Benzene)	400	55	293
			210(75)
Vinyl chloride (900)	7.2	50	5.1
Vinyl chloride(Benzene)	10	22	5.8
Vinyl chloride(Methylene chloride)	11	30	6.8
			5.9(0.9)
Vinyl chloride(63% humidity)	1.9	45	1.3
Methylene chloride (2,200)	230	91	180
Methylene chloride(Benzene)	140	74	105
Methylene chloride (63% humidity)	5.4	188	4.6

[a] Sampling cartridge: 13 mm i.d. x 60 mm in length sorbent bed, 7.96 mL sorbent.

[b] Number of theoretical plates for 60 mm sorbent bed, air at 24°C, and linear velocity 13.3 cm/sec.

[c] Sampling volume, Raymond-Guiochon relationship. In parentheses, standard deviation.

Table 51. SAMPLING VOLUMES AT 24°C: POLYIMIDES PI-109, PI-115 AND PI-149[a]

Sorbent	Compound(challenge)	50% BV, L	N[b]	SV, L[c]
PI-109	Vinyl chloride (-)	26	48	18
	Vinyl chloride(Methylene chloride)	26	30	16
	Vinyl chloride(benzene)	32	20	18
				17(1)
	Vinyl chloride (63% humidity)	10	68	7.8
	Methylene chloride (-)	204	73	156
	Methylene chloride (63% humidity)	23	47	16
PI-115	Vinyl chloride (-)	12	18	6.3
	Vinyl chloride(Methylene chloride)	10	19	5.4
	Vinyl chloride(Benzene)	11	19	6.1
				5.9(0.5)
	Vinyl chloride (63% humidity)	3.2	68	2.4
	Methylene chloride (-)	91	8	26
	Methylene chloride (63% humidity)	16	23	9.3
PI-149	Vinyl chloride (-)	11	17	5.7
	Vinyl chloride (Methylene chloride)	11	38	7.3
	Vinyl chloride (Benzene)	12	13	5.3
				6.1(1.1)
	Vinyl chloride (63% humidity)	2.6	74	2.0
	Methylene chloride (-)	100	24	62
	Methylene chloride (63% humidity)	16	11	6.3

[a] Sampling cartridge: 13 mm i.d. x 60 mm in length sorbent bed, 7.96 mL sorbent.

[b] Number of theoretical plates for 60 mm sorbent bed, air at 24°C, and linear velocity 13.3 cm/sec.

[c] Sampling volume, Raymond-Guiochon relationship. In parentheses, standard deviation.

Table 52. BACKGROUND OF SORBENT CARTRIDGES VS. STORAGE TIME

Sorbent	Background (total integrated area x 10^{-3}, a.u.)					Observations
	0	2	4	6	8 weeks[a]	
Tenax GC®	140 140 140(9)	650 444 550(206)	260 180 220(81)	3,230[b] 230 230	1,150 570 860(577)	
PI-119	1,700 1,200 1,450(500)					Too high initial background
PI-109 A.	2,000 500 1,300 1,400(781)					Too high initial background
PI-109 B.	36 36 36(0)	High[c]				Background increasing in time
PI-115	473 289 380(184)	119[d] 315 220(196)	537[e] 347 442(190)			Acceptable background, relatively stable in time.

[a] Individual values and mean (range or standard deviation).

[b] Contamination of unknown origin.

[c] Not quantitatively evaluated, ghost peaks (spikes) and flame off several times.

Table 53. RECOVERY AND SHELF LIFE OF TENAX GC® CARTRIDGES

Peak	RRT	Area x 10^{-3}	ID
0 Weeks			
1	0.50	18	CH_3Cl (?)
	0.44	14	
2	0.53	12	CH_2CHCl (?)
	0.45	11	
3	0.55	15	CH_3SH (?)
	0.47	9	
4	0.54	12	
	0.50	8	
5	0.61	45	CH_2Cl_2
	0.56	33	
6	0.65	25	
	0.61	12	
7	0.67	12	
	0.62	11	
8	0.68	44	$CHCl_3$
	0.64	26	
9	1.00	18	C_6F_6
		16	
10	1.24	16	$C_6F_5CF_3$
	1.31	14	
11	1.33	24	C_6H_6
	1.40	61	
4 Weeks			
1	0.29	2.8	CH_3Cl (?)
	0.32	1.3	
2	0.31	18.6	CH_2CHCl (?)
	0.35	9.6	
3	0.32	9.7	CH_3SH (?)
	0.34	9.7	
4	-	-	
5	0.57	31	CH_2Cl_2
	0.59	12	
6-8	-	-	

(continued)

Table 53 (Cont'd.)

Peak	RRT	Area x 10^{-3}	ID
4 Weeks (cont'd)			
9	1.00	15	C_6F_6
		17	
10	1.29	20	$C_6F_5CF_3$
	1.32	21	
11	1.38	106	C_6H_6
	1.40	181	
6 Weeks			
1-2	-	-	
3	0.44	54	CH_2CHCl and CH_3SH (?)
	0.45	70	
4	0.49	26	
	0.50	22	
5	0.57	64	CH_2Cl_2
	0.57	48	
6	0.58	20	
	0.58	22	
7	0.63	25	
	0.63	30	
8	0.65	37	$CHCl_3$
	0.66	39	
9	1.00	25	C_6F_6
		26	
10	1.18	18	$C_6F_5CF_3$
	1.19	22	
11	1.37	98	C_6H_6
	1.38	100	

Table 54. RECOVERY AND SHELF LIFE OF SORBENT CARTRIDGES: PI-109

Peak	RRT	Area x 10^{-3}	ID
0 Weeks			
1	0.43	34	CH_3Cl
	0.49	19	
2	0.45	55	CH_2CHCl
	0.51	95	
3	0.46	116	CH_3SH
	0.54	28	
4	0.49	300	CH_2Cl_2 and Propylene oxide (?)
	0.60	131	
5	0.56	85	
	0.62	70	
6	0.57	35	
	0.64	46	
7	0.59	54	
	0.66	104	
8	0.66	62	$CHCl_3$
	-	-	
9	1.00	77	C_6F_6
		38	
10	1.02	16	$ClCH_2CH_2OH$
	1.01	17	
11	1.17	39	$C_6F_5CF_3$
	1.14	26	
12	1.22	220	C_6H_6
	1.20	172	

Table 55. RECOVERY AND SHELF LIFE OF SORBENT CARTRIDGES: PI-115

Peak	RRT	Area x 10^{-3}	ID
0 Weeks			
1	0.38	15	CH_3Cl
	0.38	8	
2	0.42	22	CH_2CHCl
	0.42	15	
3	0.44	284	CH_3SH and Propylene oxide (?)
	0.43	276	
4	0.56	106	CH_2Cl_2
	0.56	144	
5	0.58	32	
	0.57	76	
6	0.59	34	$CHCl_3$
	0.59	89	
7	0.63	59	
	0.63	30	
8	0.67	49	
	0.68	37	
9	1.00	62	C_6F_6
		75	
10	1.02	20	$ClCH_2CH_2OH$
	1.03	15	
11	1.16	44	$C_6F_5CF_3$
	1.18	76	
12	1.21	243	C_6H_6
	1.23	308	
2 Weeks			
1	0.38	65	CH_3Cl
	0.40	57	
2	0.41	75	CH_2CHCl
	0.42	63	
3	0.44	140	CH_3SH
	0.44	98	
4	0.45	88	
	0.46	82	
5	0.55	103	CH_2Cl_2
	0.56	92	

(continued)

Table 55 (Cont'd.)

Peak	RRT	Area x 10^{-3}	ID
2 Weeks (cont'd)			
6	0.65	55	$CHCl_3$
	0.65	71	
7	1.00	88	C_6F_6
		74	
8	1.02	19	$ClCH_2CH_2OH$
	1.01	9	
9	1.18	50	$C_6F_5CF_3$
	1.20	61	
10	1.23	281	C_6H_6
	1.25	173	

The "time zero" cartridges for PI-109 gave much more intense early eluting peaks, and seven compounds were identified by matching retention times. Propylene oxide probably coeluted with methylene chloride. Three compounds-- acrolein, methanol, and acrylonitrile--could not be unequivocally identified. After two weeks of storage the background was too high. Overall, PI-109 is a very promising sorbent, but the problem of a high background has to be solved. This might be accomplished by simply using high purity starting materials in the synthesis.

For PI-115, the "time zero" chromatograms revealed intense early eluting peaks. The general profiles of the chromatograms were similar to those of PI-109. The results of the cartridges stored for 2 weeks were close to the "time zero" ones. After 4 weeks of storage, the background was too high to complete the analysis. PI-115 had a better background, being stable up to two weeks. Its adsorption properties were not as good as PI-109. Overall, the best polyimide sorbent tested was PI-115. Nevertheless, improving the background of the sorbent would be desirable.

Electron Microscopy of Selected Sorbents

The scanning electron micrographs of Tenax GC® and polyimides PI-109 and PI-115 are presented in Figures 25 to 27.

The morphology indicated by the electron micrograph was consistent with surface area measurements by mercury intrusion porosimetry (~70 m^2/g for Tenax GC®, ~60 m^2/g for PI-115, and ~70 m^2/g for PI-109).

The nature of the surface available for adsorption appears different for all three sorbents. Uniform pore sizes are characteristic for Tenax. PI-115 appears to have a considerable amount of fibrillar structure, a rather unexpected feature. PI-109 has a considerable amount of microporosity. This fact and the higher polarity of the polymeric chemical structure explains its higher retention for low molecular weight compounds.

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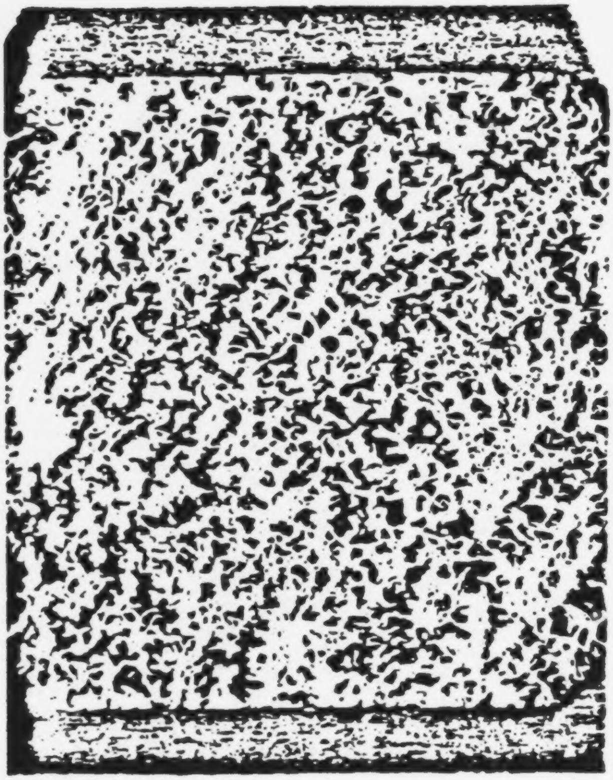

Figure 25. Scanning electron micrograph of Tenax GC® sorbent (1750X).

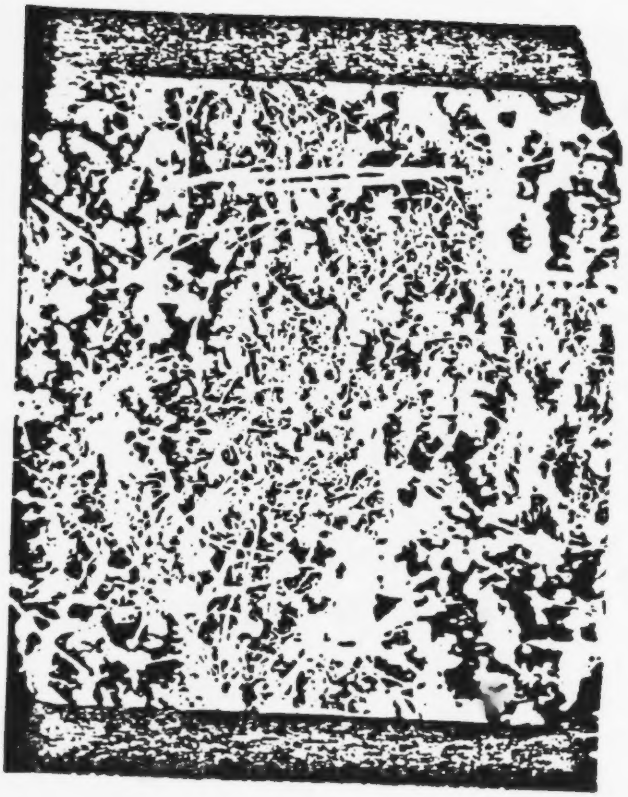

Figure 26. Scanning electron micrograph of polyimide PI-115 (1750X).

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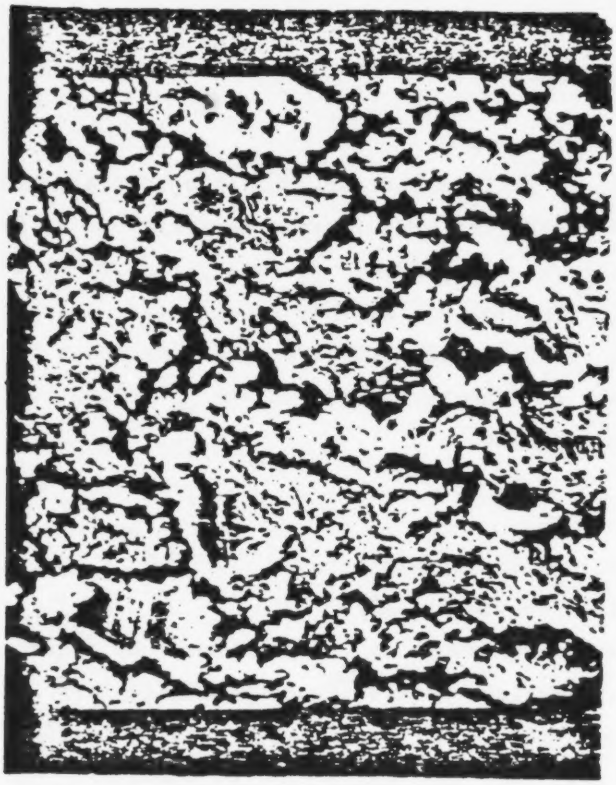

Figure 27. Scanning electron micrograph of polyimide PI-109 (1750X).

SECTION 8

CORRELATIONS BETWEEN POLYMER STRUCTURE AND ADSORPTION PROPERTIES OF SORBENTS

THERMODYNAMIC PARAMETERS OF ADSORPTION

Adsorption Coefficients

For all the discussions in this Section, the experimental data were provided by the Level II isothermal measurements as described in Section 6.

The study of retention time dependence vs. analyte quantity defined a region (<1 μg) where the retention was maximum and constant. This was a necessary and sufficient condition that the adsorption isotherm of the solute was linear; the dependence of adsorbed solute on the gas phase concentration of solute is given by Henry's law:

$$C_s = K_D \cdot C_g$$

where:

C_s = concentration of adsorbed solute, moles/m^2;
K_D = distribution constant, cm^3/m^2;
C_g = concentration of solute in the gas phase, moles/cm^3.

In a gas-chromatography elution experiment exhibiting ideal behavior, the net retention volume of the solute is directly related to the distribution constant. There are several ways to express this dependence.

$$V_g^T = A_s \cdot R \cdot T \cdot K_A$$

where:

V_g^T = specific retention volume at column temperature, mL/g;
A_s = specific surface area of the sorbent, m^2/g;
R = gas constant, 6.3 x 10^4 mL·mm/mole·K;
T = column temperature, K;
K_A = adsorption coefficient (Henry's Law), moles/mm·m^2.

The adsorption coefficient K_A has a similar meaning to K_D, only the units are different. Using the net retention volumes at a given column temperature for sample size <1 μg (Table G-1) their temperature dependence is:

$$\log V_N^T = a + b \times \frac{1}{T}$$

The net retention volumes at 20°C and specific retention volumes (20°C, in mL/g, dividing by the weight of the sorbent in the GC column) were calculated. Then, using the above relationship, the adsorption coefficients were also calculated.

The amount of solute retained by a unit weight of the sorbent for a fixed concentration in the gas phase which obeys Henry's law is given by:

$$q_g = \frac{K_A \cdot A_s \cdot c_g \cdot (760\ \text{mmHg}) \cdot (MW)}{10^6}$$

where:

q_g = grams solute retained at saturation by 1 g sorbent;

c_g = concentration of solute in the gas-phase, ppm.

We calculated the q_g values for a 1 ppm gas-phase concentration for the test compounds. The net retention volumes at 20°C, specific retention volumes at 20°C, adsorption coefficients and q_g (1 ppm) values for all Level II test solutes on Tenax GC®, PI-109, PI-119, PI-149, and PI-140 (PI-115) are listed in Table 56.

The retention volumes for n-octane on PI-109 and PI-140(PI-115) were very low, and the number of theoretical plates of the elution peaks was also low. A molecular sieving effect may have been operative. The value of the apparent cross-sectional area for the n-octane molecule, derived by Kiselev[8], is 61.0 A^2; the same parameter for benzene is 40.3 A^2. All other test substances were smaller molecules. The surface area versus pore size distribution curves derived by mercury intrusion porosimetry also suggested (see Section 7) that a considerable amount of microporosity is present in polyimide sorbents.

The pyridine retention times on all polyimide sorbents were very large. The plots of log V_N^T vs. temperature were not linear. The physical adsorption-retention model for pyridine on polyimide sorbents differs from other chemicals. If the Henry's law relationships for K_A and q_g (1 ppm) were inadvertently calculated for pyridine adsorption, unrealistically high values would be obtained (listed in parenthesis in Table 56).

The specific retention volumes for all test substances were one to two orders of magnitude greater for polyimide sorbents relative to Tenax GC®. The specific surface areas being comparable, the capacity of polyimide sorbents

$$\log V_N^T = a + b \times \frac{1}{T}$$

The net retention volumes at 20°C and specific retention volumes (20°C, in mL/g, dividing by the weight of the sorbent in the GC column) were calculated. Then, using the above relationship, the adsorption coefficients were also calculated.

The amount of solute retained by a unit weight of the sorbent for a fixed concentration in the gas phase which obeys Henry's law is given by:

$$q_g = \frac{K_A \cdot A_s \cdot c_g \cdot (760 \text{ mmHg}) \cdot (MW)}{10^6}$$

where:

q_g = grams solute retained at saturation by 1 g sorbent;

c_g = concentration of solute in the gas-phase, ppm.

We calculated the q_g values for a 1 ppm gas-phase concentration for the test compounds. The net retention volumes at 20°C, specific retention volumes at 20°C, adsorption coefficients and q_g (1 ppm) values for all Level II test solutes on Tenax GC®, PI-109, PI-119, PI-149 and PI-140 (PI-115) are listed in Table 56.

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The specific retention volumes for all test substances were one to two orders of magnitude greater for polyimide sorbents relative to Tenax GC®. The specific surface areas being comparable, the capacity of polyimide sorbents

Table 56. NET RETENTION VOLUMES, SPECIFIC RETENTION VOLUMES, ADSORPTION COEFFICIENTS AND SOLUTE - SORBENT SATURATION CONCENTRATIONS

Solute	MW	V_N^{20}, mL	V_g^{20}, mL/g	K_A (moles/mm.m^2)	q_g, g/g (C_g = 1 ppm)
Tenax GC® (A_s = 69 m^2/g; w_s = 0.41 g/column)					
Acetonitrile	41.05	1,390	3,380	2.6×10^{-6}	5.7×10^{-6}
Acrolein	56.07	1,670	4,070	3.2×10^{-6}	9.4×10^{-6}
Benzene	78.12	28,560	69,400	5.4×10^{-5}	2.2×10^{-4}
1,2-Dichloroethane	98.96	20,090	48,800	3.8×10^{-5}	2.0×10^{-4}
Ethanol	46.07	740	1,800	1.4×10^{-6}	3.4×10^{-6}
Methyl ethyl ketone	72.12	17,400	42,370	3.3×10^{-5}	1.3×10^{-4}
Nitromethane	61.04	4,230	10,290	8.0×10^{-6}	2.6×10^{-5}
n-Octane	114.23	7.67×10^5	1.865×10^6	1.4×10^{-3}	8.8×10^{-3}
Propylene oxide	56.07	1,630	3,970	3.1×10^{-6}	9.2×10^{-6}
Pyridine	79.10	7.63×10^4	1.85×10^5	1.4×10^{-4}	6.0×10^{-4}
Vinyl chloride	62.50	277	674	5.2×10^{-7}	1.7×10^{-6}
PI-109 (A_s = 73 m^2/g; w_s = 1.02 g/column)					
Acetonitrile		1.6×10^5	1.6×10^5	1.2×10^{-4}	2.7×10^{-4}
Acrolein		1.2×10^5	1.2×10^5	8.6×10^{-5}	2.7×10^{-4}
Benzene		4.1×10^5	4.0×10^5	3.0×10^{-4}	1.3×10^{-3}
1,2-Dichloroethane		4.8×10^5	4.8×10^5	3.5×10^{-4}	1.9×10^{-3}
Ethanol		1.2×10^5	1.2×10^5	8.8×10^{-5}	2.2×10^{-4}

(continued)

Table 56 (Cont'd.)

Solute	MW	V_N^{20}, mL	V_g^{20}, mL/g	K_A (moles/mm.m^2)	q_g, g/g (C_g = 1 ppm)
PI-109 (A_s = 73 m^2/g; w_s = 1.02 g/column) (cont'd.)					
Methyl ethyl ketone		8.3×10^5	8.2×10^5	6.0×10^{-4}	2.4×10^{-3}
Nitromethane		2.4×10^5	2.4×10^5	1.8×10^{-4}	5.9×10^{-4}
n-Octane		$2.1 \times 10^{5*}$	$2.1 \times 10^{5*}$	$1.5 \times 10^{-5*}$	$9.8 \times 10^{-4*}$
Propylene oxide		8.7×10^4	8.6×10^4	6.4×10^{-5}	2.0×10^{-4}
Pyridine		3.6×10^7	3.5×10^7	$(2.6 \times 10^{-2**})$	$(1.1 \times 10^{-1**})$
Vinyl chloride		4.5×10^3	4.4×10^3	3.3×10^{-6}	1.1×10^{-5}
PI-119 (A_s = 144 m^2/g; w_s = 0.27 g/column)					
Acetonitrile		1.3×10^5	4.9×10^5	1.8×10^{-4}	8.3×10^{-4}
Acrolein		3.0×10^5	1.1×10^6	4.1×10^{-4}	2.5×10^{-3}
Benzene		3.6×10^5	1.3×10^6	4.9×10^{-4}	4.2×10^{-3}
Dichloroethane		6.4×10^5	2.3×10^6	8.8×10^{-4}	9.5×10^{-3}
Ethanol		9.6×10^4	3.5×10^5	1.3×10^{-4}	6.6×10^{-4}
Methyl ethyl ketone		2.3×10^6	8.3×10^6	3.1×10^{-3}	2.5×10^{-2}
Nitromethane		4.1×10^5	1.5×10^6	5.6×10^{-4}	3.7×10^{-3}
Octane		8.6×10^6	3.1×10^7	1.2×10^{-2}	1.5×10^{-1}
Propylene oxide		1.4×10^5	5.3×10^5	2.0×10^{-4}	1.2×10^{-3}
Pyridine		1.7×10^{11}	6.2×10^{11}	$(2.3 \times 10^{2**})$	$(2.0 \times 10^{3**})$
Vinyl chloride		2.9×10^3	1.0×10^4	3.9×10^{-6}	2.7×10^{-5}

(continued)

Table 56 (Cont'd.)

Solute	MW	V_N^{20}, mL	V_g^{20}, mL/g	K_A (moles/mm.m^2)	q_g, g/g (C_g = 1 ppm)
PI-149 (A_s = 29 m^2/g***, w_s = 0.44 g/column)					
Acetonitrile		1.1×10^5	2.5×10^5	4.6×10^{-4}	4.2×10^{-4}
Acrolein		8.0×10^4	1.8×10^5	3.4×10^{-4}	4.2×10^{-4}
Benzene		5.5×10^5	1.2×10^6	2.3×10^{-3}	4.0×10^{-3}
1,2-Dichloroethane		6.2×10^6	1.4×10^6	2.6×10^{-3}	5.8×10^{-3}
Ethanol		8.3×10^4	1.9×10^5	3.5×10^{-4}	3.6×10^{-4}
Methyl ethyl ketone		1.6×10^6	3.6×10^6	6.7×10^{-3}	1.1×10^{-2}
Nitromethane		2.7×10^5	6.1×10^5	1.1×10^{-3}	1.5×10^{-3}
n-Octane		1.4×10^6	3.1×10^6	5.8×10^{-3}	1.5×10^{-2}
Propylene oxide		6.2×10^4	1.4×10^5	2.6×10^{-4}	3.3×10^{-4}
Pyridine		1.1×10^9	2.6×10^9	(4.8**)	(8.4**)
Vinyl chloride		2.5×10^3	5.6×10^3	1.0×10^{-5}	1.4×10^{-5}
PI-140(115) (A_s = 53 m^2/g; w_s = 1.38 g/column)					
Acetonitrile		2.0×10^5	1.5×10^5	1.5×10^{-4}	2.5×10^{-4}
Acrolein		3.3×10^5	2.4×10^5	2.5×10^{-4}	5.6×10^{-4}
Benzene		1.1×10^6	8.2×10^5	8.3×10^{-4}	2.6×10^{-3}
1,2-Dichloroethane		1.9×10^5	1.4×10^5	1.4×10^{-4}	5.6×10^{-4}
Ethanol		7.1×10^5	5.2×10^5	5.3×10^{-4}	9.8×10^{-4}
Methyl ethyl ketone		3.0×10^6	2.2×10^6	2.2×10^{-3}	6.4×10^{-3}
Nitromethane		3.5×10^5	2.6×10^5	2.6×10^{-4}	6.5×10^{-4}

(continued)

Table 56 (Cont'd.)

Solute	MW	V_N^{20}, mL	V_g^{20}, mL/g	K_A (moles/mm.m^2)	q_g, g/g (C_g = 1 ppm)
PI-140(115) (A_s = 53 m^2/g; w_s = 1.38 g/column)					
n-Octane		$1.4 \times 10^{4*}$	$1.0 \times 10^{4*}$	$1.0 \times 10^{-6*}$	$4.8 \times 10^{-6*}$
Propylene oxide		9.5×10^{4}	6.9×10^{4}	7.0×10^{-5}	1.6×10^{-4}
Pyridine		1.4×10^{8}	10.0×10^{7}	$(1.0 \times 10^{-1**})$	$(3.2 \times 10^{-1**})$
Vinyl chloride		4.8×10^{3}	3.5×10^{3}	3.5×10^{-6}	8.9×10^{-6}

* Retention too low.

** Chemisorption, Henry's law does not apply.

*** For batch PI-1001.

surface for specific and nonspecific interaction with solutes was significantly higher. This trend was reflected also in the adsorption coefficients K_A and in the solute-in-sorbent saturation concentrations q_g.

The specific retention volumes for some solutes studied here can be compared with literature data (Table 57). The agreement was satisfactory, taking into account a number of objective and subjective limitations. The data from R.F. Gallant's work[9] may be more accurate, but still the solute concentration in the gas chromatographic measurements was not given and there is no experimental proof given that the solutes were at concentrations which obeyed Henry's law.

The data of Butler and Burke[10] were not corrected for the pressure drop across the GC column, and it is not clear whether the listed retention volumes were calculated at room temperature or at column temperature. The data that Brown and Purnell reported were derived at unknown solute concentrations and were extrapolated net retention volumes at room temperature[11].

The limitation in any comparison of this sort is the batch to batch variation in sorbent properties. Gallant[9] reported a specific surface area of 29.5 m^2/g for the Tenax GC® used, a mean value of experimental nitrogen adsorption porosimetric data, and other literature data. The specific surface area of Tenax GC® used here was 69.5 m^2/g, measured by mercury intrusion porosimetry (see Section 6). The uncertainty in specific surface area measurements were in the 10 to 20% range, as suggested by inter- and intra-laboratory reproducibility (see Section 6). Taking into account the limitations listed above, the agreement between the data presented here and Gallant's[9] data for K_A and q_g is satisfactory (Table 58).

Even the chemical nature of Tenax GC® apparently has changed with time. The Tenax currently available is insoluble in methylene chloride, in contrast to Tenax available in 1974, which was soluble[12].

Adsorption Enthalpy

The adsorption enthalpy can readily be calculated from retention data, using the relationship:

$$\log V_g^T = -\Delta H_{ads}/2.303RT + \text{constant}$$

If the retention data are independent of concentration, then the calculated adsorption enthalpy is constant over this concentration range and equivalent

Table 57. COMPARISON OF SPECIFIC RETENTION VOLUMES ON TENAX GC® WITH LITERATURE DATA

Solute	V_g^{20}, mL/g (1)	(2)	(3)	(4)
Acetonitrile	3.4×10^3	-	4.0×10^3	3.9×10^3
Benzene	6.9×10^4	6.1×10^4	8.3×10^4	6.2×10^4
1,2-Dichloroethane	4.9×10^4	2.3×10^4	-	5.5×10^4
Ethanol	1.8×10^3	9.1×10^2	-	1.8×10^3
Methyl ethyl ketone	4.2×10^4	2.2×10^4	4.1×10^4	3.3×10^4
_n_-Octane	1.9×10^6	1.9×10^5	-	7.7×10^5
Vinyl chloride	6.7×10^2	-	-	3.1×10^2

(1) This work.

(2) R. F. Gallant, J. W. King, P. L. Levins, J. F. Piecewicz, Characterization of Sorbent Resins for Use in Environmental Sampling, EPA 600/7-78-054, March 1978, p. 22.

(3) L. D. Butler, M. F. Burke, J. Chromatogr. Sci., 14, 117 (1976); listed as log V_g^{20}.

(4) R. H. Brown, C. J. Purnell, J. Chromatogr., 178, 79 (1980); listed as V_R as 20°C, for a column holding 0.13 g Tenax GC®.

Table 58. COMPARISON OF ADSORPTION COEFFICIENTS AND SOLUTE - SORBENT SATURATION CONCENTRATIONS WITH LITERATURE DATA (TENAX GC®)

Solute	K_A, moles/mm.m^2 (20°C)		q_g, g/g (C_g = 1 ppm)	
	(1)	(2)	(1)	(2)
Benzene	5.4×10^{-5}	1.4×10^{-4}	2.2×10^{-4}	2.0×10^{-4}
1,2-Dichloroethane	3.8×10^{-5}	5.4×10^{-5}	2.0×10^{-4}	-
Ethanol	1.4×10^{-6}	2.1×10^{-6}	3.4×10^{-6}	-
Methyl ethyl ketone	3.3×10^{-5}	5.1×10^{-5}	1.3×10^{-4}	-
n-Octane	1.4×10^{-3}	4.4×10^{-4}	8.8×10^{-3}	9.0×10^{-4}

(1) This work.

(2) R. F. Gallant, J. W. King, P. L. Levins, J. F. Piecewicz, Characterization of Sorbent Resins for Use in Environmental Sampling, EPA 600/7-78-054, March 1978, 70, 73.

to the theoretical value of "adsorption enthalpy at zero surface coverage". Outside Henry's law region the adsorption enthalpy is dependent on sorbent surface coverage and probably approaches the vaporization enthalpy for multilayered adsorption.

Using specific retention volumes at a column temperature independent of solute concentration, we derived a linear relationship by using the least squares procedure of the following form:

$$\log V_g^T = a + b \times \frac{1}{T}$$

The adsorption enthalpy at zero surface coverage is:

$$-\Delta H_{ads} = 2.303 \times R \times b \quad \text{(cal/mole)}$$

$R = 1.989$ cal/mole·K, the gas constant.

The calculated adsorption enthalpies are listed in Table 59. The standard errors of the adsorption enthalpies derived from the linear fit, with few exceptions, were in the range of 50 to 300 cal/mole which compares very favorable with the thermodynamic uncertainty of the calculated values, i.e., equal to the thermal energy R x T (583 cal/mole at 20°C).

The adsorption enthalpies of pyridine on polyimide sorbents, except for PI-109, are high or very high, which is characteristic for a chemisorption. The pyridine sorption process probably involves specific interaction with the uncapped carboxylic terminal groups of the polymers which would yield salt formation.

The n-octane adsorption enthalpies for Tenax GC®, PI-119, and PI-149 appear to be abnormally high. For polyimides PI-109 and PI-140, the adsorption enthalpies are in the expected range, but the specific retention volumes are very low, and we suspect that a molecular-sieving effect has occurred. A hypothesis for PI-119 and PI-149 can be offered. A significant contribution to adsorption may have occurred with pores with "activated entry", i.e., pores were not small enough to exclude n-octane completely, but still small in comparison to the solute molecule which required an "activation energy" for entering the pore. This hypothesis explains two divergent behaviors:

(1) PI-109 and PI-140: low retention, normal adsorption enthalpy and

(2) PI-119 and PI-149: normal retention, high adsorption enthalpy. This classification is based on the microporosity of the polyimide sorbent. But it is only a hypothesis since the experimental proof is lacking. For the abnormally high adsorption enthalpy of n-octane on Tenax GC®, an explanation is not readily apparent.

The magnitude of the difference between the adsorption enthalpy (ΔH_{ads}) and the vaporization enthalpy (ΔH_v) for the same solute is a measure of the specific interaction between that solute and the sorbent.

Differences between adsorption and vaporization enthalpies at zero surface coverage by the solutes are listed in Table 60. The n-octane data exhibited the same trend as the ΔH_{ads} listed in Table 59. The pyridine data for PI-119, PI-140, and PI-149 clearly indicated that the pyridine retention on these sorbents is a chemisorption process.

Excluding the n-octane data, we calculated the correlation coefficient for the differences between ΔH_{ads} and ΔH_v[14]:

$$r = \frac{\mathrm{cov}(X_1,X_2)}{s_{X_1} s_{X_2}}$$

where:

$X_1 = -(\Delta H_{ads}-\Delta H_v)$ sorbent A for solute 1,2....,10;

$X_2 = -(\Delta H_{ads}-\Delta H_v)$ sorbent B for solute 1,2,...,10;

COV = covariance;

s = standard deviation.

The matrix of calculated correlation coefficients is presented in Table 61. Inspection of the correlation coefficient matrix, the sorbents can be divided into three groups:

(A) Tenax GC®, dissimilar to PI-109, PI-119, PI-149, and very dissimilar to PI-140;

(B) PI-109, PI-119, PI-149, dissimilar to Tenax GC® and dissimilar to PI-140;

(C) PI-140(115).

The nature of the interactions of the test solutes for all the above defined sorbent groups was different and can be related to the chemical nature of polymers as follows:

(A) Tenax GC®, chemically a poly(2,5-diphenyl-p-phenylene) oxide, the adsorption sites are aromatic mononuclear in nature, the more polar ether (oxygen atoms) groups are sterically hindered and essentially inaccessible by solutes; interactions with adsorbed compounds are primarily by dispersion (London) forces, relatively small polar interaction forces, as illustrated by small $-(\Delta H_{ads}-\Delta H_v)$ values.

Table 59. ADSORPTION ENTHALPIES AT ZERO SURFACE COVERAGE

Solute	$-\Delta H_{ads}$ ± standard error, Kcal/mole, on sorbent:				
	Tenax GC®	PI-109	PI-119	PI-140(115)	PI-149
Acetonitrile	11.7 ± 0.1	14.0 ± 0.2	14.8 ± 0.2	15.1 ± 0.1	14.9 ± 0.2
Acrolein	12.0 ± 0.2	13.9 ± 0.1	17.7 ± 0.2	16.9 ± 0.1	14.9 ± 0.2
Benzene	14.7 ± 0.1	14.3 ± 0.1	16.2 ± 0.2	16.8 ± 0.2	16.8 ± 0.2
1,2-Dichloroethane	14.5 ± 0.1	14.5 ± 0.2	17.0 ± 0.2	13.9 ± 0.5	16.8 ± 0.1
Ethanol	12.6 ± 0.1	14.9 ± 0.2	16.4 ± 0.2	19.9 ± 1.0	16.3 ± 0.1
Methyl ethyl ketone	15.1 ± 0.3	15.5 ± 0.3	19.2 ± 0.2	19.0 ± 0.2	18.9 ± 0.1
Nitromethane	13.1 ± 0.1	13.7 ± 0.1	16.1 ± 0.1	15.2 ± 0.3	15.5 ± 0.1
_n_-Octane	19.7 ± 0.1[a]	12.0 ± 1.2	21.6 ± 0.1[a]	12.1 ± 1.7	18.5 ± 0.5[a]
Propylene oxide	12.5 ± 0.2	14.0 ± 0.2	18.0 ± 0.5	15.1 ± 0.2	15.5 ± 0.0
Pyridine	15.0 ± 0.2	19.7 ± 1.6	27.1 ± 3.2[b]	22.0 ± 1.0[b]	26.3 ± 0.3[b]
Vinyl chloride	11.8 ± 0.2	11.4 ± 0.1	14.1 ± 0.3	13.0 ± 0.2	12.6 ± 0.1

[a] Abnormally high.

[b] Possibly chemisorption.

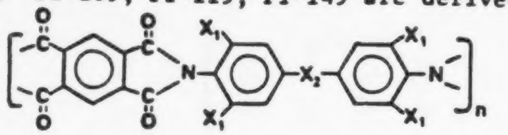
Table 60. DIFFERENCES BETWEEN ADSORPTION ENTHALPIES AND VAPORIZATION ENTHALPIES

Solute	ΔH_v Kcal/mole (lit.6)	$-(\Delta H_{ads}-\Delta H_v)$, Kcal/mole, for sorbent:				
		Tenax GC	PI-109	PI-119	PI-140	PI-149
Acetonitrile	8.2	3.5	5.9	6.7	7.0	6.8
Acrolein	7.6	4.4	6.2	10.1	9.2	7.3
Benzene	8.2	6.6	6.2	8.1	8.6	8.6
1,2-Dichloroethane	7.9	6.5	6.6	9.1	5.9	8.8
Ethanol	9.7	3.0	5.2	6.7	10.2	6.6
Methyl ethyl ketone	8.2	7.0	7.3	11.0	10.8	10.7
Nitromethane	9.2	3.8	4.5	6.9	6.0	6.3
n-Octane	9.2	10.5*	2.8	12.4*	2.9	9.3*
Propylene oxide	7.3	5.2	6.7	10.7	7.8	8.2
Pyridine	9.6	5.3	9.0	17.4**	12.3**	16.7**
Vinyl chloride	6.3	5.6	5.2	7.8	6.7	6.30

*Abnormally high.

**Probably chemisorption.

(B) PI-109, PI-119, PI-149 are derived from bicyclic diamines:

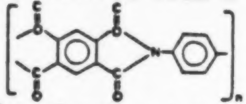


$X_1 = H, CH_3$

$X_2 = O, CH_2, SO_2$

with a considerably more polar surface, capable of specific polar interactions with solute molecules (dipole-dipole, dipole-induced dipole);

(C) PI-140, derived from a monocyclic diamine:



capable of polar interaction but also hydrogen-bond interaction with solute molecules. The hydrogen bonding capability of the sorbent can be related to a more mobile π-electron system (in bicyclic diamines the x_2 between the phenyl groups interrupts the π-electron conjugation), or maybe to a different orientation of the carbonyl groups relative to the polymer crystalite surface.

Additional insight into solute-sorbent interactions can be gleened from correlations between retention data and solubility parameters.

USING SPECIFIC RETENTION VOLUME DATA

The Solubility Parameter Concept

The solubility parameter concept originated from the work of Hildebrand and Scatchard on the nature of liquid state and solutions[15,16]. The original definition of the solubility parameter was in terms of molar cohesive energy per unit volume of a liquid:

$$\delta = (-E^c/V_m)^{1/2}$$

where:

$-E^c$ = molecular cohesive energy, cal/mole;

V_m = molar volume, cm^3/mole;

δ = solubility parameter, $cal^{1/2} \cdot cm^{-2/3}$.

The cohesive energy is the sum of molecular interactions which can be broadly classified as dispersive (London) forces, orientation (dipole-dipole and dipole-induced dipole) forces, and hydrogen bonding.

Experimentally, the cohesive energy can be determined from vaporization enthalpies extrapolated to a common temperature (25°C), and assuming ideal gas behavior of solute vapors:

$$-E^c = \Delta H_v^{298} - RT$$

$$\delta = (\Delta H_v^{298} - RT)^{1/2}/V_m^{1/2}$$

The expansion of the solubility parameter to include dispersion, orientation and hydrogen bonding terms follows a semi-empirical approach. The "total" solubility parameter is defined as the squared sum of the "partial" solubility parameters, and it is not necessarily equal to δ as defined above:

$$\delta_T = (\delta_d^2 + \delta_o^2 + \delta_h^2)^{1/2} \neq \delta$$

Semi-empirical solubility parameter expanded scales were derived by Hansen[17], Karger[18] and others[19].

For practical application, the solubility parameter was used originally to predict mutual solubilities of two compounds as an extension of the old concept of "like dissolves like". The mutual solubility is at maximum if the solubility parameters are matching one another.

Generally, a macroscopic property related to a pairwise interaction (solubility, adsorption, etc.) is related functionally to a difference $(\delta_a-\delta_b)$ or a sum $(\delta_a+\delta_b)$ of solubility parameters.

Correlations of Specific Retention Volumes with Solubility Parameters

In a gas-solid chromatography elution experiment and in the framework of the linear-ideal model[20], the specific retention volume is directly related to the distribution constant of the solute between the mobile and the stationary phase:

$$V_s^T = K_D = C_s/C_m$$

where:

V_s^T = specific retention volume at column temperature, mL/m^2;
K_D = distribution constant of the solute, mL/m^2;
C_s = concentration in stationary phase, $moles/m^2$;
C_m = concentration in the mobile phase, moles/mL.

If the specific retention volumes are measured at low solute concentrations and are independent of concentration, the distribution constant is equivalent to Henry's law constant for the solute-sorbent pair and is a true equilibrium constant. The thermodynamic equation relating the equilibrium constant to the thermodynamic excess functions is applicable:

$$-RT \ln K_D = \Delta G^E = \Delta H^E - T\Delta S^E = \Delta E^E + P\Delta V^E - T\Delta S^E$$

where:

R = gas constant;
T = absolute temperature, °K;
ΔG^E = excess free energy;
ΔH^E = excess enthalpy;
ΔS^E = excess entropy;
ΔE^E = excess energy;
ΔV^E = volume change for transfer of solute from mobile to stationary phase.

If it is further assumed that the entropy of mixing is ideal, and the change of volume on mixing is zero, then

$$RT \ln K_D = -\Delta E^E$$

According to the expanded solubility parameter model of Karger, Snyder, and Eon[21], the excess energy for adsorption in gas-solid chromatography can be expressed as:

$$\Delta E^E(\text{adsorption}) \alpha A^i(\delta_d^i \cdot \delta_d^a + \delta_o^i \cdot \delta_o^a + \delta_a^i \cdot \delta_b^a + \delta_b^i \cdot \delta_a^a)$$

where:

index i = solute;
index a = adsorbent;
δ_d = dispersion solubility parameter;
δ_o = hydrogen bond acceptor solubility parameter;
δ_b^a = hydrogen bond donor solubility parameter;
A^i = molar area (area occupied by a monomolecular layer of a mole) of the solute.

Combining the later equation with the relationships between V_s^T, K_D and ΔE^E:

$$\log V_s^T \alpha A^i(\delta_d^i \cdot \delta_d^a + \delta_o^i \cdot \delta_o^a + \delta_a^i \cdot \delta_b^a + \delta_b^i \cdot \delta_a^a)$$

The functional relationship between specific retention volumes at 20°C and the solubility parameters of the solute used was:

$$\log V_s^{20} = a + b \times (A^i \cdot \delta^i)$$

where:

V_s^{20} = specific retention volume at 20°C;
A^i = molar area of the solute, cm^2/mole;
δ^i = solute solubility parameter, $(cal/mL)^{1/2}$.

The molar area of solute was calculated using a relationship proposed by Emmett and Brunauer[22]:

$$A^i = 1.091.N^{1/3}.(M/\delta)^{2/3} \text{ (cm}^2\text{/mole)}$$

The solubility parameters were calculated using reported physical constants (vaporization enthalpies, densities, and molecular weights) and are listed in Table 62.

We preferred the solubility parameter values calculated here since literature values for all test compounds were not available. We preferred to use a consistent set of data for correlation analysis.

The coefficients of the regression lines were calculated by the least squares procedure[23] and are listed together with standard error of the slope, correlation coefficients, Fischer's F, and significance levels in Table 63. These data are graphically depicted in Figures 28 to 32.

Retention data for n-octane and pyridine were not examined since the n-octane data are erratic and pyridine data reflected a chemisorption process.

Except for PI-140, the ethanol and acrolein data points are outliers. The Student t-test, when applied to the hypothesis that the data points do not follow the linear calculated regression, was significant at the 0.05 level. This is consistent with the conclusion that for adsorption enthalpies (except for PI-140), hydrogen bonding is not an important mechanism in solute retention.

From Karger's theoretical relationship:

$$\log V_s^{20} = k\cdot\delta^a(A^i\cdot\delta^i) + \text{constant}$$

the slope b from the correlation lines can be related to an experimental solubility parameter of the adsorbent:

$$\delta^a = b/k$$

The value of the proportionality constant 1/k is unknown but can be approximated using a calculated solubility parameter, to "anchor" the scale.

The solubility parameter of Tenax GC® was calculated using atomic and group contributions[24], and then the experimental solubility parameters for the polyimide sorbents were derived. These calculated values are listed in Table 64.

Tenax GC®, PI-109, and PI-140 all have solubility parameters in the same range; for PI-119 and PI-149, the solubility parameters are significantly

Table 61. MATRIX OF CORRELATION COEFFICIENTS FOR DIFFERENCES BETWEEN ADSORPTION VAPORIZATION ENTHALPIES

	Tenax GC®	PI-109	PI-119	PI-149	PI-140(115)
Tenax GC®	1.000	0.478	0.357	0.406	0.084
PI-109	0.478	1.000	0.928	0.935	0.686
PI-119	0.358	0.928	1.000	0.939	0.684
PI-149	0.406	0.935	0.939	1.000	0.712
PI-140(115)	0.084	0.686	0.684	0.712	1.000

Table 62. PHYSICAL CONSTANTS OF TEST SOLUTES

Solute	MW, daltons	δ, g/cm^3 (20°C)	δ[a] (cal/ml)$^{1/2}$	A^{i}[b] cm^2/mole	Solubility Parameter[c] (cal/mL)$^{1/2}$
Acetonitrile	41.05	0.786	12.0	1.26×10^9	11.9
Acrolein	56.07	0.841	10.3	1.61×10^9	-
Benzene	78.12	0.876	9.2	1.80×10^9	9.2
1,2-Dichloroethane	98.96	1.235	9.6	1.68×10^9	-
Ethanol	46.07	0.789	12.5	1.36×10^9	12.7
Methyl ethyl ketone	72.12	0.805	9.2	1.81×10^9	9.3
Nitromethane	61.04	1.137	12.7	1.28×10^9	12.7
Propylene oxide	58.08	0.859[d]	10.0	1.50×10^9	-
Vinyl chloride	62.50	0.911	9.1	1.51×10^9	-

[a] Calculated, see text.

[b] Calculated, see text.

[c] Lit. 12.

[d] 0°/4°C.

Table 63. LINEAR REGRESSION $\log V_a^{20}$ VERSUS $A^i \cdot \delta^i$

Sorbent	n[a]	Slope $\times 10^{10}$	Standard Error of the slope $\times 10^{10}$	Intercept	Correlation coefficient	F	α
Tenax GC®	7	6.60	1.0	-8.15	0.943	40.2	<0.01
PI-109	7	6.71	0.95	-7.16	0.946	42.8	<0.01
PI-119	7	8.00	1.2	-8.81	0.933	33.5	<0.01
PI-149	7	8.43	0.85	-9.09	0.967	71.8	<0.01
PI-140	9	6.72	0.88	-7.14	0.899	29.7	<0.01

[a] Number of data points.

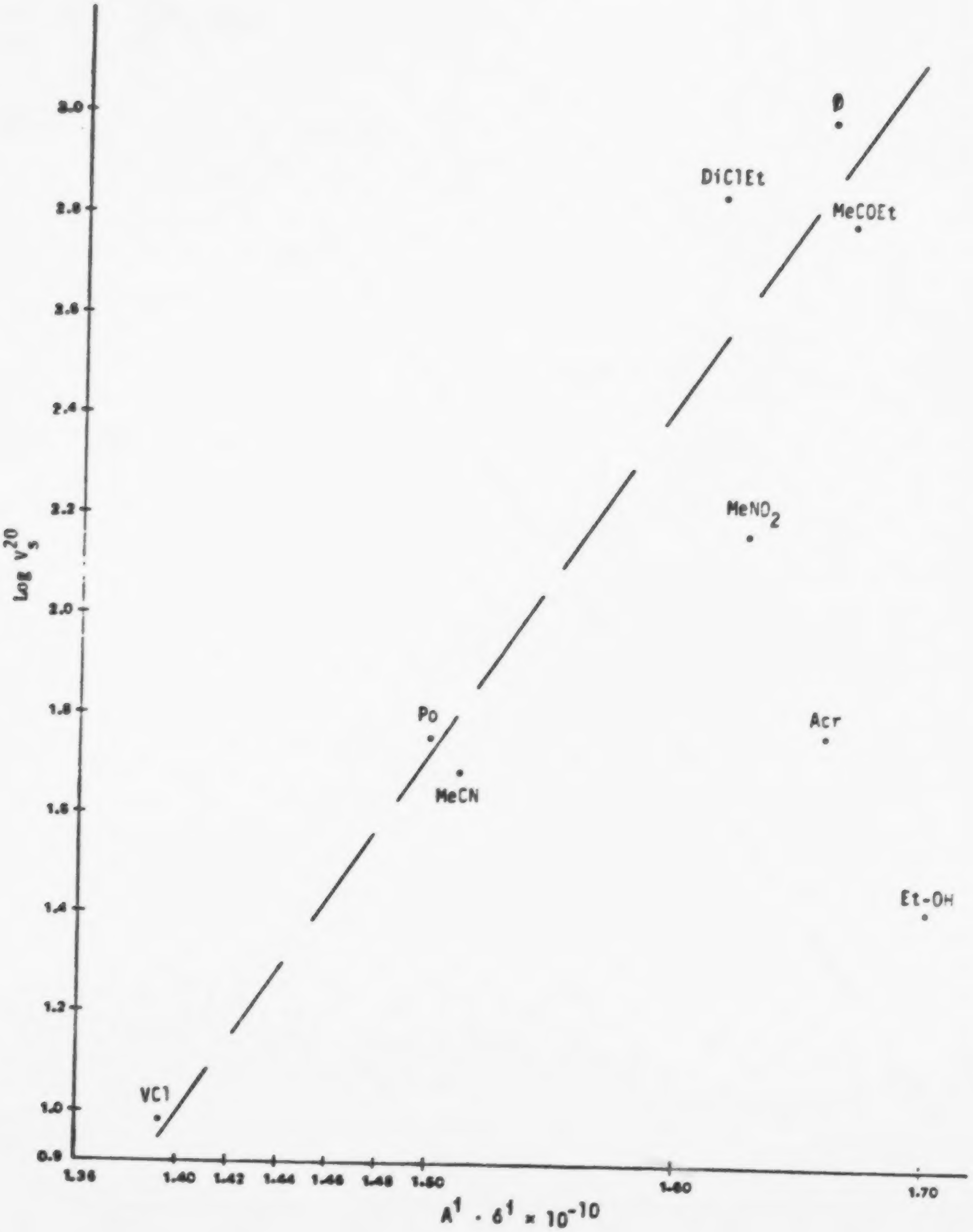


Figure 28. Log V_s^{20} versus $A^i \cdot \delta^i$ for Tenax GC®.

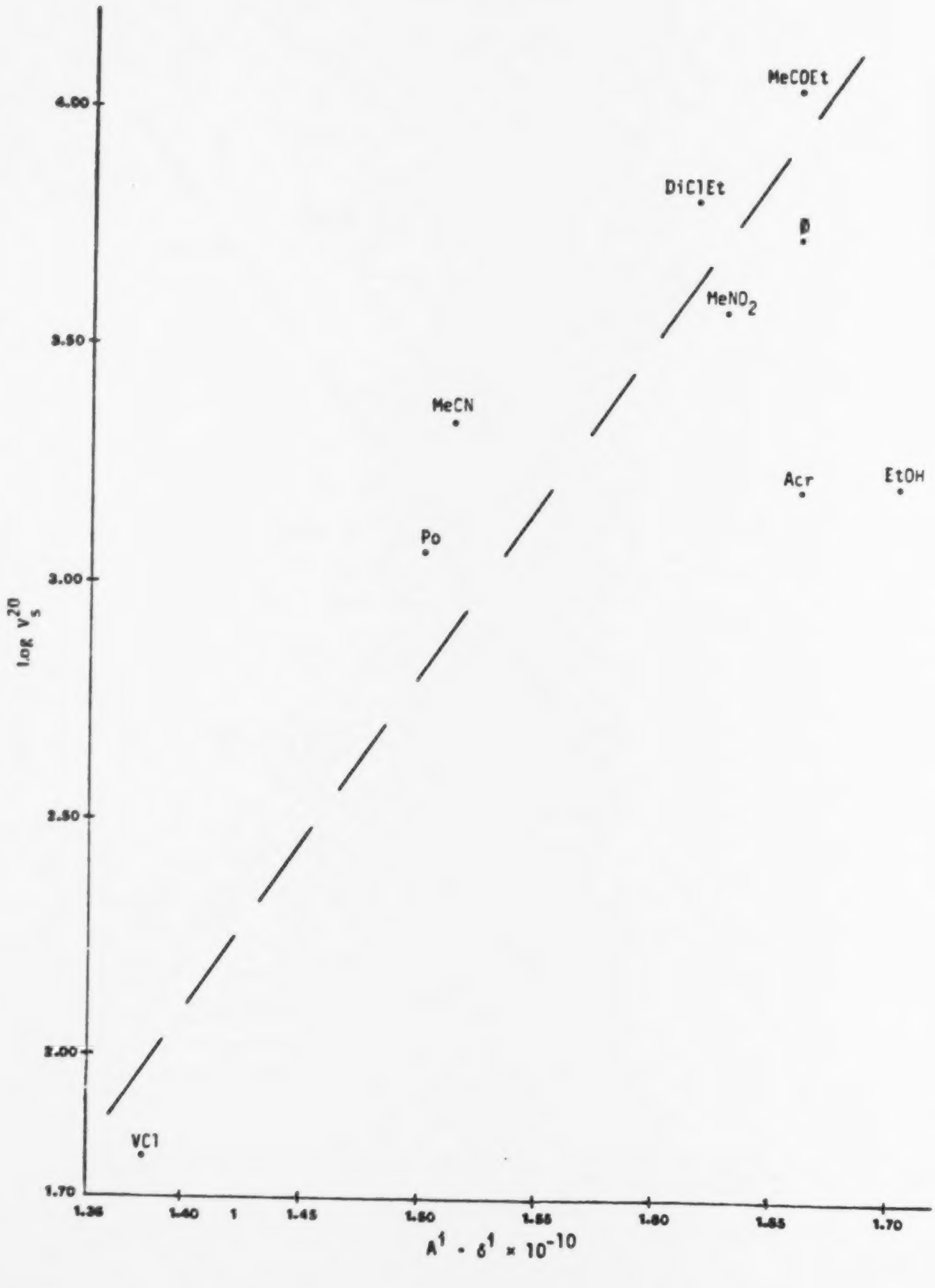


Figure 29. Log V_s^{20} versus $A^i \cdot \delta^i$ for PI-109.

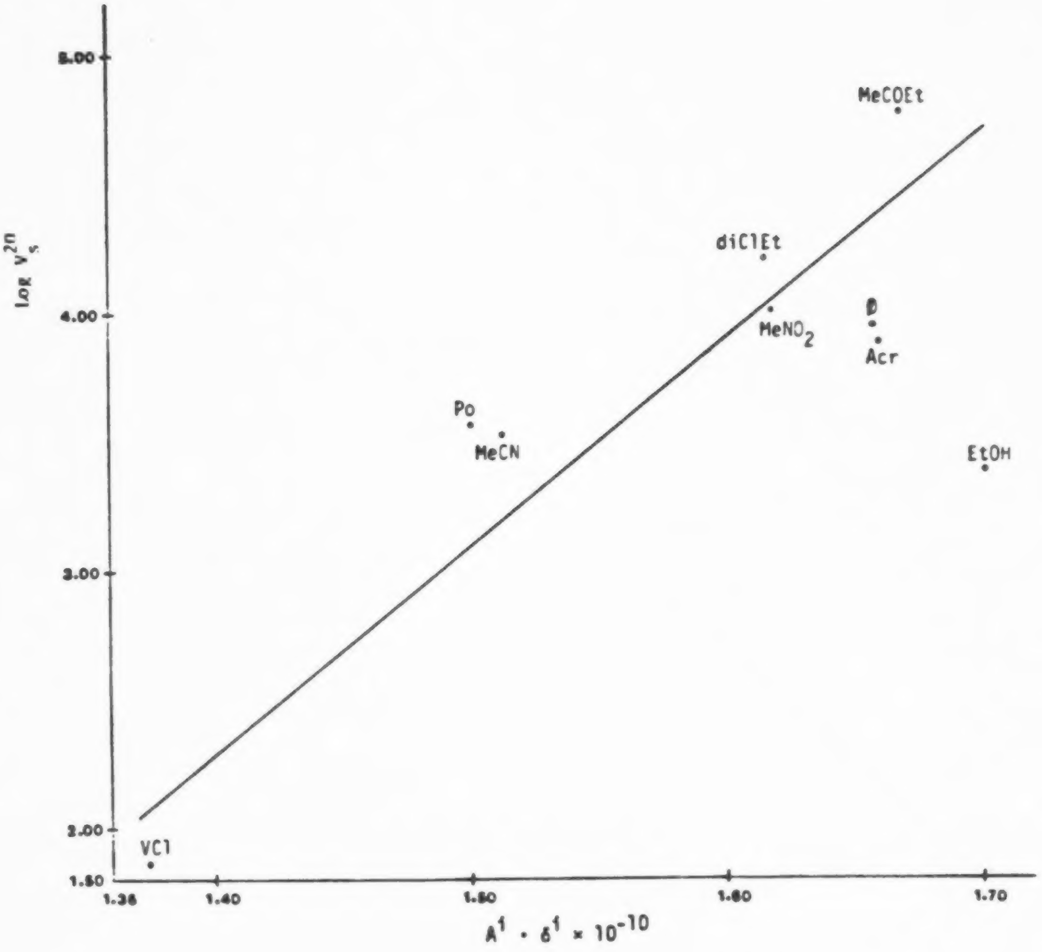


Figure 30. Log V_s^{20} versus $A^i \cdot \delta^i$ for PI-119.

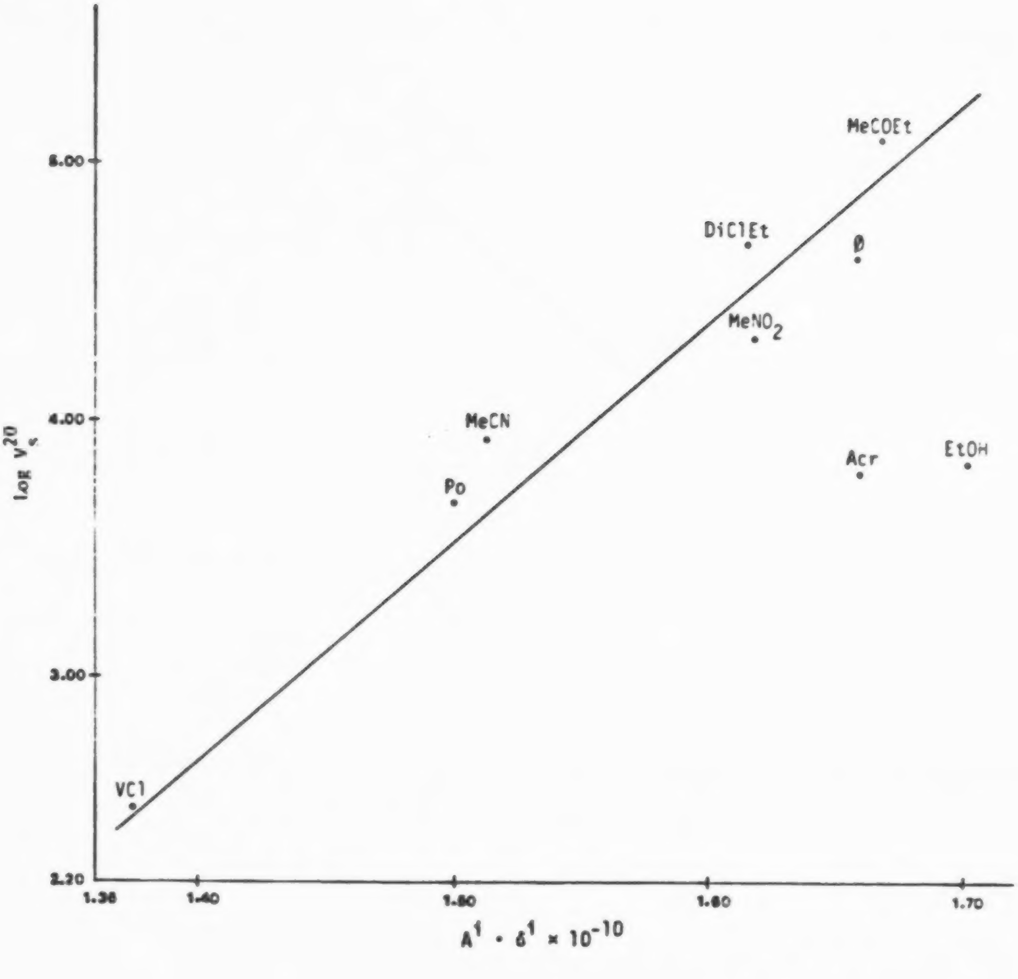


Figure 31. Log V_s^{20} versus $A^i \cdot \delta^i$ for PI-149.

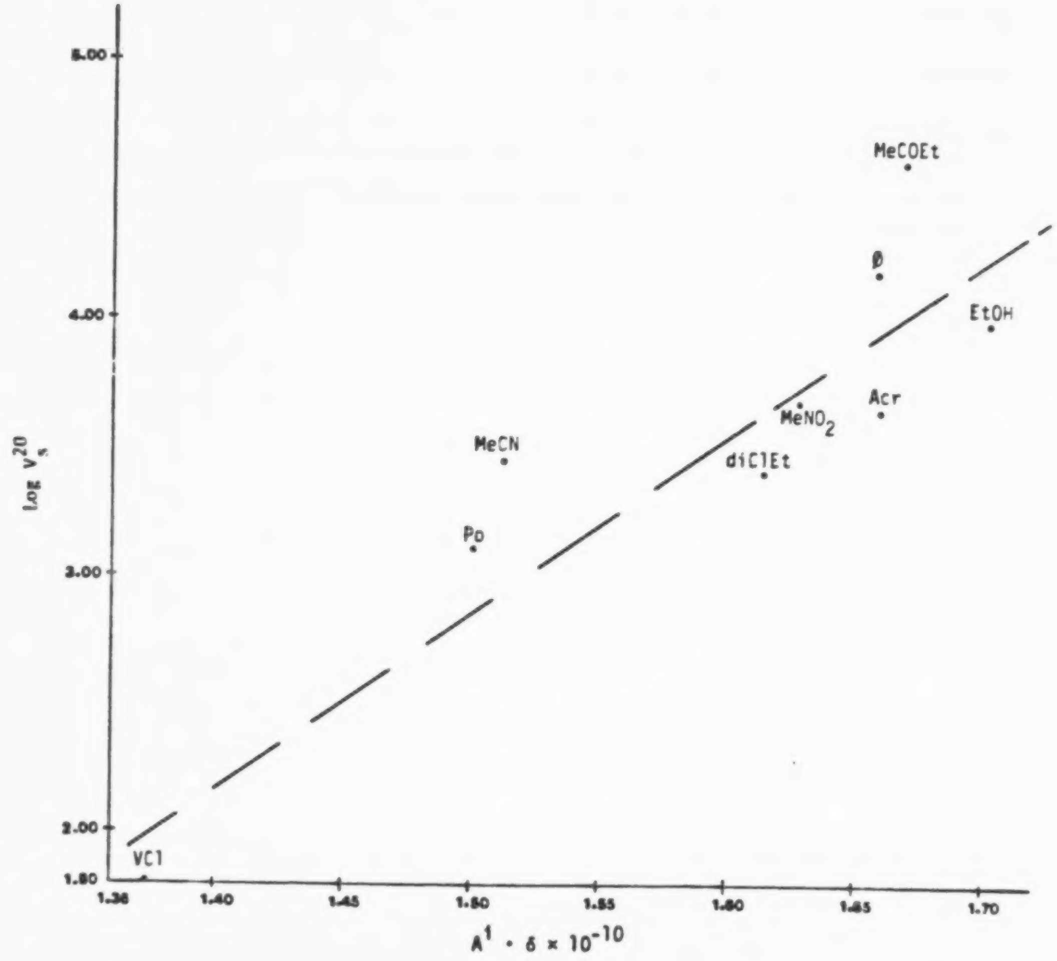


Figure 32. Log V_s^{20} versus $A^i \cdot \delta^i$ for PI-140(115).

Table 64. SORBENT SOLUBILITY PARAMETERS

Sorbent	$(k \cdot \delta^a \pm SE) \times 10^{10}$	Solubility Parameter ± SE
Tenax GC®	6.6 ± 1.0	11.1[a]
PI-109	6.7 ± 0.95	11.3 ± 1.6
PI-119	8.0 ± 1.2	13.5 ± 2.0
PI-149	8.4 ± 0.85	14.2 ± 1.4
PI-140(115)	6.7 ± 0.88	11.3 ± 1.5

[a] "Anchor" value, calculated from atom and group contributions.

higher. The calculated regression lines can be used to predict retention volumes (vide infra); more importantly, this prediction leads to a clue as to which chemical structure in a polymer is needed for maximizing adsorption of a compound or class of compounds.

Multiple Correlations of Specific Retention Volumes with Expanded Solubility Parameters

The Karger-Snyder-Eon model[21] for adsorption in gas-solid chromatography utilizes expanded solubility parameters for solutes, and principally allows the calculation of expanded (dispersion, orientation and hydrogen bonding) solubility parameters of the sorbent. The first limitation in using this model is related to the availability of expanded solubility parameters for solutes. Because the expanded solubility parameters are semi-empirical in nature, it is imperative to use an internally consistent set of values. The most complete list of solubility parameters includes only five of the test solutes[12] used in this testing program. These values are listed in Table 65. With five data points, only a regression with three variables can be calculated; for this the Hansen's expanded scale (three values) and not Karger's scale was used (four values, including δ_a-acceptor and δ_b-donor-hydrogen bond solubility parameters).

From a statistical point of view, we are near the validity/invalidity limits of the statistical model. Thus, a significance level of 0.25 was chosen, a fairly large value. The following multiple regression relationship was used:

$$Y = b_1 \cdot X_1 + b_2 \cdot X_2 + b_3 \cdot X_3 + a$$

where:

$Y = \log V_s^{20}$;

$X_1 = A^i \cdot \delta_d^i \cdot 10^{-10}$;

$X_2 = A^i \cdot \delta_o^i \cdot 10^{-10}$;

$X_3 = A^i \cdot \delta_h^i \cdot 10^{-10}$;

$b_1 = k \cdot \delta_d^a \cdot 10^{10}$;

$b_2 = k \cdot \delta_o^a \cdot 10^{10}$;

$b_3 = k \cdot \delta_h^a \cdot 10^{10}$;

index a = adsorbent;

index i = solute;

Table 65. EXPANDED SOLUBILITY PARAMETERS OF SOLUTES

Solute	Solubility Parameters, $(cal/ml)^{1/2}$			
	δ_T[a]	δ_d[b]	δ_o[c]	δ_h[d]
Acetonitrile	12.0	7.5	8.8	3.0
Benzene	9.1	9.0	0	1.0
Ethanol	13.0	7.7	4.3	9.5
Methyl ethyl ketone	9.3	7.8	4.4	2.5
Nitromethane	12.3	7.7	9.2	2.5

[a] Total solubility parameter, $(\delta_d^2 + \delta_o^2 + \delta_h^2)^{1/2}$.

[b] Dispersion solubility parameter.

[c] Orientation (polar) solubility parameter.

[d] Hydrogen bonding solubility parameter.

d = dispersion;

o = orientation;

h = hydrogen bonding.

The regression coefficients, their standard errors, correlation coefficients, Fischer's F, and significance levels for the multiple correlation and for regression coefficients were calculated and are listed in Table 66.

From the calculated set of regression coefficients, expanded solubility parameters for the polyimide sorbents were derived, again using Tenax GC® as the "anchor". The supplementary constraint was:

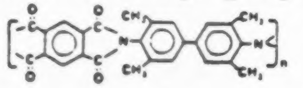
$$(\delta_d^2+\delta_o^2+\delta_h^2)^{1/2}_{\text{Tenax GC}^{®}} = 11.1$$

The calculated sorbent solubility parameters are listed in Table 67. When the significance level of the corresponding regression coefficient was higher than 0.25, a zero value is given.

Within the limited constraints of the statistical model, the standard errors of the calculated solubility parameters were quite large. However, some interesting observations should be noted. Again, the only sorbent exhibiting all three interaction appears to be PI-140(115) while only the contribution of the hydrogen bond term being statistically significant.

For PI-109, PI-119, and PI-149 two interactions mechanisms were evident. The dispersion and polar terms were statistically significant. The highest value for the orientation (polar) solubility parameter of PI-119 was consistent with the presence in its structure of a strongly polar group ($-SO_2-$).

The dispersion solubility parameter of PI-109 was the lowest, and it may be attributed to the presence of methyl groups in the structure:



A dispersion interaction with the solutes may be the main operating mechanism for Tenax GC® while the polar term contribution is not significant.

The general implications of a multiple regression of the retention volumes versus expanded solubility parameters leads to the same grouping of the sorbents as did the analysis of adsorption enthalpies (A - Tenax GC®; B - PI-140; and C - PI-109, PI-119, PI-149). It should be stressed that the former analysis used intercepts of retention versus temperature regressions, and the latter analysis used the slopes of the lines. The strong coincidence of the two analyses lends to the internal consistency of the model used.

Table 66. MULTIPLE REGRESSION OF LOG V_s^T VERSUS EXPANDED SOLUBILITY PARAMETERS

	Tenax GC	PI-109	PI-119	PI-149	PI-140 (115)
Correlation Coefficient					
R_Y, 123	0.974	0.981	0.977	0.972	0.974
F	6.27	8.37	7.12	5.68	6.06
Significance Level, α	0.25	0.25	0.25	0.25	0.25
Regression Coefficients					
b_1	2.57	2.06	3.66	3.25	2.99
SE[a]	1.20	0.51	0.89	0.96	0.80
F	4.57	16.42	16.88	11.36	13.83
α	0.10...0.25	0.10...0.25	0.10...0.25	0.10...0.25	0.10...0.25
b_2	0.37	1.47	2.05	1.62	1.25
SE[a]	0.70	1.03	0.52	0.56	0.47
F	0.91	12.0	15.70	8.29	7.12
α	>0.25	0.10...0.25	0.10...0.25	0.10...0.25	0.10...0.25
b_3	-0.42	0.16	0.38	0.20	0.81
SE[a]	0.47	0.12	0.35	0.38	0.31
F	0.79	0.60	1.08	0.54	6.63
α	>0.25	>0.25	>0.25	>0.25	0.10...0.25

[a] Standard error.

Table 67. EXPANDED SORBENT SOLUBILITY PARAMETERS

Sorbent	Solubility Parameter ± Standard Error, $(cal/mL)^{1/2}$			
	δ_T[a]	δ_d[b]	δ_o[c]	δ_h[d]
Tenax GC®	11.1[e]	10.6 ± 5.0	0	0
PI-140(115)	13.9 ± 2.3	12.4 ± 3.3	5.2 ± 1.9	3.4 ± 1.3
PI-109	9.5 ± 1.7	8.5 ± 2.1	4.3 ± 1.2	0
PI-119	17.4 ± 3.0	15.1 ± 3.7	8.5 ± 2.2	0
PI-149	15.1 ± 3.3	13.5 ± 4.0	6.7 ± 2.3	0

[a] Total solubility parameter, $(\delta_d^2 + \delta_o^2 + \delta_h^2)^{1/2}$.

[b] Dispersion solubility parameter.

[c] Orientation (polar) solubility parameter.

[d] Hydrogen bonding solubility parameter.

[e] "Anchor value".

In general, a correlation analysis of retention data using solubility parameters has great potential. Even when a very limited set of input data are used, very interesting correlations between chemical structure and adsorption properties of sorbents can be drawn.

Correlations of Specific Retention Volumes with Solute Polarity Scales

One of the very active fields in Quantitative Structure-Activity Relationships (QSAR) involves solvent effects. This concept provides an explanation and prediction of changes in rates and equilibria of reactions versus solvent change. A number of "solvent polarity scales" were derived, the solubility parameter scale being one of them.

A brief list of solvent polarity scales widely used included:

- Dimroth's E_T[25];
- Braunstein's S[26];
- Brooker's x_r[27];
- Kamlet-Taft's π[28].

The polarity index of a particular solvent has been derived, usually, from experimental data in a model reaction or equilibrium. For example, solvatochromic shifts (bathochromic or hypsochromic shifts of the lowest frequency UV-vis absorption band) of 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide dye, for the E_T scale.

Most of the solvent polarity scales have been derived from model "reactions" in which the Lewis type acidity or basicity of the solvent is the important and dominant property. Kamlet-Taft's π scale is a more balanced one, reflecting mainly the polarity of the solvents, excluding, as much as possible, hydrogen bonding and acid-base properties (Lewis or Brönsted type).

Carr[29] has shown that a linear relationship existed between the Kamlet-Taft's π and a simple function, θ, of the solvent dielectric constant. He advocated the use of the θ scale in solvent effect studies.

The θ function has the form:

$$\theta = \frac{3D\cdot \ln D}{D\,\ell n D - D + 1} - \frac{6}{\ln D} - 2$$

D = solvent dielectric constant.

A theoretical "orientation solubility parameter" can be estimated by:

$$\delta_0^{th} = 173\,\frac{\mu}{V_m}\sqrt{\theta} \qquad (\mathrm{cal}^{1/2}\ \mathrm{mL}^{-1/2})$$

where:

δ^{th} = theoretical orientation solubility parameter;

μ^{o} = dipole moment of the solvent, Debye;

V_m = molar volume, mL/mole;

The advantage of Carr's approach is the derivation of the solvent polarity index from physical characteristics like dielectric constant and dipole moment, and not from a "model reaction" which may not be related to the property under study.

A two term linear model correlation was examined in our study for the specific retention volumes on polyimide sorbents:

$$\log V_s^{20} = D + O + \text{residuals}$$

D = dispersion interaction term;

O = orientation (polar) interaction term.

For the orientation term, Carr's approach, which is a derivation of solute polarity index from the θ function, was used. For the first term, D (dispersion interaction term), the approach used retention data for solutes on graphitized carbon black. Extensive studies by Kiselev[23] demonstrated that the solute retention on graphitized carbon black was essentially dependent only on the dispersion interaction between solute and the graphite surface (stationary phase). Unfortunately, few retention data on graphitized carbon black for solutes are available in the literature (see Table 68).

The solubility parameter correlations (vide infra) had shown that the retention on Tenax GC® was also dependent on the dispersion interaction. Thus, the specific retention of the solutes on Tenax GC® was used as estimates of D.

The linear model was:

$$\log V_s^{20} = k_1 \cdot \log V^{20}_{s(\text{Tenax GC}^{®})} + k_2 \cdot (A^i \cdot \delta_o^{th}) + k_3$$

The input data for PI-109 and the two-parameter linear regression results are listed in Table 69. The physical constant needed for δ_o^{th} and A^i derivation are listed in Table 70. The orientation (polar) interaction terms contribution was not statistically significant and; therefore, the two term linear model failed.

Nevertheless, this model may still be useful, but it requires:

(1) better estimates for the D term (dispersion interaction); for example, specific retention times on graphitized carbon black, measured under the same experimental parameters as the Level II specific retention times determined in this project;

Table 68. SOLUTE RETENTION ON GRAPHITIZED CARBON BLACK

Solute	$V_s^{100°C}$, mL/m^2 [a]	R_T, min[b]
Benzene	1.70	3.35
1,2-Dichloroethane	0.48	1.20
Ethanol	0.14	0.62
Methyl ethyl ketone	-	1.55

[a] Lit. 30.

[b] On Carbopack C, at 125°C, lit. 34.

Table 69. PHYSICAL CONSTANTS OF THE SOLUTES: TWO PARAMETER LINEAR MODEL FOR SPECIFIC RETENTION VOLUMES

Solute	μ[a]	D[b]	θ[c]	V_m[d]	δ_o^{th}[e]	A_m[f]
Acetonitrile	3.94	-	0.446[g]	52.2	8.47	22.1
Acrolein	3.12	18.5	0.383	66.7	5.01	26.0
Benzene	0	2.3	0.130	89.2	0	31.6
1,2-Dichloroethane	0	10.6	0.326	80.1	0	29.4
Ethanol	1.69	24.3	0.408	58.4	3.20	23.8
Methyl ethyl ketone	2.70	18.5	0.383	89.5	3.23	31.7
Nitromethane	3.46	-	0.448[g]	53.7	7.46	22.5

[a] Debye, lit. 31.

[b] Lit. 32.

[c] Calculated.

[d] In mL/mole.

[e] Calculated, in $\mathrm{cal}^{1/2}\cdot\mathrm{mL}^{-1/2}$.

[f] Calculated, in $\mathring{A}^2$/molecule, lit. 22.

[g] Lit. 29.

Table 70. TWO PARAMETERS LINEAR MODEL FOR SPECIFIC RETENTION VOLUMES ON POLYIMIDE SORBENTS

$\log V_s^{20} = k_1\cdot\log V_{s(\text{Tenax GC}^{®})}^{20}+k_2\cdot(A_m^i\cdot\delta_o^{th})+k_3$

Solute	$\log V_{s(\text{PI-109})}^{20}$	$\log V_{s(\text{Tenax GC}^{®})}^{20}$	$A_m^i\cdot\delta_o^{th}\times 10^{-2}$
Acetonitrile	3.34	1.69	1.92
Acrolein	3.20	1.77	1.30
Benzene	3.73	3.00	0
1,2-Dichloroethane	3.81	2.85	0
Ethanol	3.21	1.41	0.76
Methyl ethyl ketone	4.05	2.78	1.02
Nitromethane	3.51	2.17	1.68

Correlation coefficient, $R_{Y,12}$	0.921
F	11.25
$\alpha(2;4)$	0.01..0.05
k_1	0.52494
SE	0.128
F	16.9
$\alpha(1;4)$	0.01..0.05
k_2	0.086
SE	0.108
F	0.63
$\alpha(1;4)$	>0.25
k_3	2.295

(2) use of semi-empirical Kamlet-Taft π values as solute polarity estimates, instead of θ function derivation, if available; currently only a few π values for the test solutes used in this program are available.

PREDICTION OF RETENTION VOLUMES USING A LINEAR REGRESSION MODEL

A practical application for the calculated linear regression equations was the prediction of retention volumes for solutes which were not tested on the sorbents synthesized in this program. If, for example, the one parameter correlation with solubility parameters are used, then the necessary input data are:

(1) Solute: (a) vaporization enthalpy, cal/mole;
(b) molecular weight, daltons;
(c) density at 20°C, g/mL;

(2) Sorbent: (a) regression coefficients (a and b) in LogV_s^{20} = a+bx($A^i \cdot \delta^i$);
(b) specific surface area, m^2/g.

We calculated the retention volumes at 20°C on a Tenax GC® sorbent with 29.5 m^2/g specific surface area and compared them with experimental data listed by Gallant[9].

Example:

Toluene: $-\Delta H_v = 9{,}370$ cal/mole[13];
MW = 92.15 daltons;
$\delta = 0.8670$ g/mL.

a. The solubility parameter is:

$$\delta = (\Delta H_v - RT)^{1/2} V_m^{-1/2} = (9{,}368.5 - 293 \times 1.989)^{1/2} (92.15/0.8669)^{-1/2}$$

$$\delta = 9.1$$

b. The molar area of toluene is:

$$A = 1.091 (MW/\delta)^{2/3} N^{1/3} = 1.091 (92.15/0.8669)^{2/3} (6.023.10^{23})^{1/3}$$

$$A = 2.02 \times 10^9\ cm^2/mole$$

c. The linear relationship for specific retention volumes on Tenax GC® is: (excluding alcohols and aldehydes)

$\log V_s^{20} = 6.60 \times 10^{-10} \times A^i \delta^i - 8.15$ (for Tenax GC®);

$\log V_s^{20} = 6.60 \times 1.838 - 8.15 = 3.981$ (toluene on Tenax GC®).

d. The retention volume of toluene on Tenax GC® (29.5 m^2/g) at 20°C, in mL/g, is:

$V_g^{20} = A_s \times (\text{colog } V_s^{20}) = 29.5(\text{colog } 3.981) = 2.82 \times 10^5$ mL/g.

e. The experimental determined retention volume is[2]:

V_g^{20}(exp) = 7.88 x 10^5 mL/g.

% difference = 100(7.88 - 2.82)/7.88 = 64%

Calculated and experimental retention volumes at 20°C on Tenax GC® are listed in Table 71. The agreement was satisfactory, especially when compared with the agreement among experimental data from various authors (see Table 57). The relationship used is not applicable for alcohols and aldehydes, and n-butanol is included in Table 71 only to stress this point.

Table 71. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED RETENTION VOLUMES ON TENAX GC®

Solute	δ^i	A^i	$(A^i \cdot \delta^i) \times 10^{-10}$	V_g^{20}[a]	V_g^{20}[b]	% Difference[c]
Toluene	9.1	2.02×10^9	1.838	2.82×10^5	7.88×10^5	64
Ethylbenzene	8.4	2.22×10^9	1.865	4.25×10^5	8.36×10^5	49
Chlorobenzene	9.7	1.97×10^9	1.911	8.56×10^5	1.36×10^6	37
Trichloroethylene	9.3	1.81×10^9	1.683	2.68×10^4	8.82×10^4	70
Cyclohexanone	9.6	1.99×10^9	1.910	8.43×10^5	1.36×10^6	38
Acetophenone	9.8	2.16×10^9	2.117	1.96×10^7	1.23×10^7	-59
n-Butanol	10.7	1.83×10^9	1.958	1.75×10^6	4.34×10^4	-3,930

[a] Calculated.

[b] Experimental, lit. 9.

[c] $(V^{20}_{g(exp)} - V^{20}_{g(calc)}) \times 100/V^{20}_{g(exp)}$

SECTION 9

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APPENDIX A

GENERAL PROPERTIES OF POLYIMIDE SORBENTS

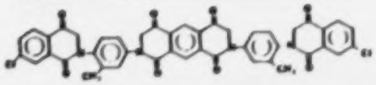
(LEVEL I DATA)

Table A1. GENERAL CHARACTERISTICS OF SORBENTS CONTAINING HALOGENS

Sorbent	Characteristics				
	Weight of Sorbent (3 ft x 2 mm i.d. column)	Density[a] (g/mL)	% Weight Loss After Conditioning	Color Change	General Observations
PI-101	2.017	0.84	7.3	rust-rust	none
PI-102	2.072	0.86	7.2	orange dark brown-brown	melted after cycling
PI-103	0.634	0.26	7.3	light orange-same	10% dead volume
PI-107	0.857	0.36	5.6	yellow-white	none
PI-108	0.821	0.34	4.4	orange gold-lighter	none
PI-201	0.972	0.40	0.2	yellow-same	none
PI-202	1.730	0.72	2.2	brown-yellow-same	melted
PI-113	1.242	0.52	7.6	light yellow-same	none
PI-114	1.983	0.83	3.6	yellow orange-yellow	none
PI-205	0.508	0.21	4.1	bright yellow-same	none
PI-206	1.652	0.69	0.1	mottled brown dark and yellow-brown	none
PI-115	1.022	0.43	0.6	sand brown-same	very high back pressure
PI-118	1.802	0.75	4.4	light yellow-same	12.5% settling
PI-213	0.824	0.34	6.9	bright yellow-same	none
PI-121	0.720	0.30	8.6	bright yellow-same	none
PI-124	0.592	0.25	4.2	pale orange-same	hard to pack
PI-126	1.479	0.62	15.7	tan-same	none

[a] Density is based on a column that held 2.4 mL of water.

Table A2. GENERAL CHARACTERISTICS OF TETRAIMIDE SORBENT

Sorbent	Characteristics				
	Weight of Sorbent (3 ft x 2 mm column)	Density[a] (g/mL)	% Weight Loss After Conditioning	Color Change After Conditioning	General Observations
 755	1.620	0.68	0.1	gray - same	none

[a] Density is based on a column that held 2.4 mL water.

Table A3. GENERAL CHARACTERISTICS OF SORBENTS CONTAINING NITROGEN

Sorbent	Weight of sorbent (3 ft x 2 mm i.d. column)	Density[a] (g/mL)	% Weight loss after conditioning	Color changes	General observations
PI-106	1.060	0.44	2.5	rust-light rust	none
PI-207	0.735	0.31	6.1	white-black	decomposed
PI-204	1.321	0.55	6.1	reddish brown → same	none
PI-117	0.618	0.26	9.5	yellow → same	10% settling
PI-129	0.490	0.20	2.2	beige → same	high back pressure
PI-130	0.433	0.18	0.8 gain	yellow-white	high back pressure
PI-132	0.890	0.37	2.5	orange-gold	none
PI-219	-	-	-	could not pack-too soft	
PI-218[a]	0.311	[b]	8.2	light yellow → tan	settling

[a] Density if based on column that held 2.4 mL water.

[b] Not enough packing material to fil column.

Table A4. GENERAL CHARACTERISTICS OF SORBENTS CONTAINING OXYGEN

Sorbent	Weight of sorbent (3 ft x 2 mm i.d. column)	Density[a] (g/mL)	% Weight loss after conditioning	Color changes	General observations
PI-120	-	-	-	too soft to pack	
PI-211	1.200	0.50 D	3.6	orange → same	none
PI-131	1.459	0.61	5.8	tan → same	none
PI-133	Too soft to pack				

[a] Density based on a column that holds 2.4 mL water.

Table A5. GENERAL CHARACTERISTICS OF SORBENTS CONTAINING SULFUR

	Characteristics				
Sorbent	Weight of Sorbent (3 ft x 2 mm i.d. column)	Density[a] (g/mL)	% Weight Loss After Conditioning	Color Change	General Observations
PI-112	0.796	0.33	0.6	green brown-same	none
PI-212	1.050	0.44	3.3	brown-same	none
PI-116	0.580	0.24	6.1	pale yellow-white	none
PI-119	0.275	0.12	16	pale yellow-same	hard to pack-electrostatic
PI-210	0.999	0.42	3.6	light yellow-gold	none
PI-125	0.661	0.28	4.2	beige-light brown	none
PI-209	0.344	0.14	13	pale yellow-yellow	texture of polymer changed after conditioning
PI-217	0.710	0.30	6.9	green yellow-gold	none

[a] Based on a glass column that holds 2.4 mL water.

Table A6. GENERAL CHARACTERISTICS OF SORBENTS WITHOUT HETEROATOMS

	Characteristics				
Sorbent	Weight of Sorbent (0.914 m x 2 mm i.d. column)	Density[a] (g/mL)	% Weight Loss after Conditioning	Color Changes	General Observations
PI-105	1.135	0.47	6.2		high back pressure
PI-109	1.019	0.42	4.7	green beige to beige	none
PI-128	0.752	0.31	14.0	light yellow→ dark yellow	none
PI-203	0.947	0.39	7.6	light orange→ dark orange	none
PI-122				Too soft to pack column	
PI-1001	1.129	0.47	2.9	yellow→same	none
PI-1002	1.119	0.47	0.9	gold→same	none
PI-214	Not enough synthesized to pack a column				
PI-215	Not enough synthesized to pack a column				
PI-142	0.501	0.21	1.4	yellow→same	none
PI-143	0.768	0.32	3.5	sand→same	many fines
PI-144	0.754	0.31	1.3	light yellow→same	none
PI-147	0.636	0.26	5.1	sand→same	none
PI-149	0.440	0.18	0.6	yellow→same	soft
PI-150	1.010	0.42	2.5	yellow→same	none
PI-146	Not enough synthesized to pack a column				
PI-134	Too soft to pack a column				
PI-152	0.572	0.24	3.8	light yellow→ same	high back pressure

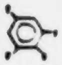
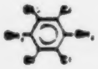
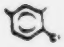
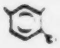
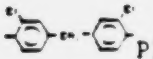
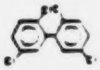
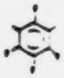
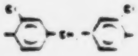
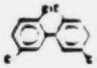
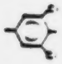
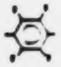
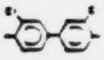
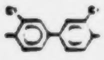
[a] Based on a column that would hold 2.4 mL water.

APPENDIX B

VOLATILE BACKGROUND OF POLYIMIDE SORBENTS

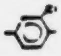
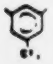
(LEVEL I DATA)

Table B1. VOLATILE BACKGROUND OF HALOGENATED SORBENTS

Sorbent	Maximum μV/sec (°C)	Plateau to °C	Peaks Retention time (min), μV
Tenax (1)	0.52(250)	170	No Peaks (NP)
Chromosorb 101	8.3(210)	146	NP
PMDA +  PI-101	2.8(263)	207	NP
PMDA +  PI-102	off scale		
PMDA +  PI-103	0.83(275)	178	NP
BTDA +  PI-201	0.58(275)	250	NP
PMDA +  PI-108	4.3(260)	235	NP
PMDA +  PI-113	1.7(275)	210	NP
PMDA +  PI-114	10(263)	114	NP
BTDA +  PI-205	0.64(275)	250	NP
BTDA +  PI-206	17(263)	137	NP
PMDA +  PI-115	4.8(268)	225	NP
PMDA +  PI-118	9.3(275)	250	NP
BTDA +  PI-213	0.33(228)	210	NP
PMDA +  PI-121	11(260)	194	NP

(continued)

Table B1 (Cont'd.)

Sorbent	Maximum µV/sec (°C)	Plateau to °C	Peaks Retention time (min), µV
PMDA +  PI-124	7.6(275)	194	NP
PMDA +  PI-126	6.1(275)	226	NP

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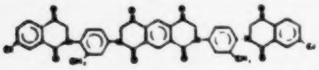
[a] NP = no peaks.

Table B2. VOLATILE BACKGROUND OF TETRAIMIDE

	Stability Measurements		
Sorbent	Maximum µV/sec (°C)	Plateau to °C	Peaks Retention Volume, µV
 755	0.72(275)	202	NP
Tenax Column 1	0.52(250)	170	NP
Tenax Column 2	0.33(270)	242	NP

[a] NP - no peak.

Table B3. VOLATILE BACKGROUND OF SORBENTS CONTAINING NITROGEN

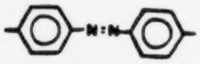
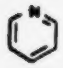
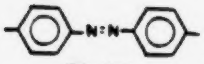
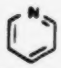
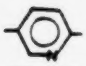
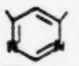
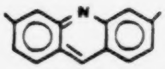
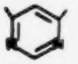
Sorbent	Maximum µV/sec (°C)	Plateau to °C	Peaks Retention Volume (mL), µV
PMDA +  PI-106	1.0(275)	242	NP
BTDA +  PI-207	5.4(275)	98	NP
BTDA +  PI-204	9.2(275)	178	NP
PMDA +  PI-117	4.2(270)	210	NP
PMDA +  PI-129	18(260)	202	NP
PMDA +  PI-130	6.7(271)	224	NP
PMDA +  PI-132	0.18(275)	210	NP
BTDA +  PI-218	7.2(264)	194	NP
Tenax (1)	0.52(250)	170	NP
Tenax (2)	0.33(270)	242	NP

Table B4. VOLATILE BACKGROUND OF SORBENTS CONTAINING OXYGEN

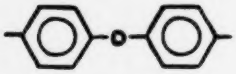
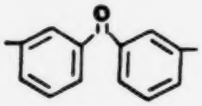
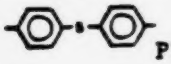
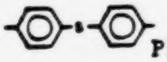
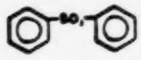
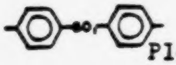
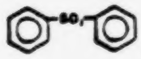
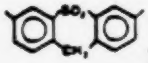
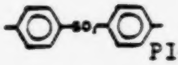
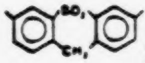
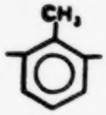
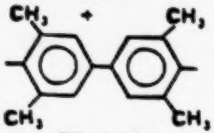
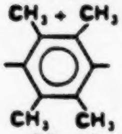
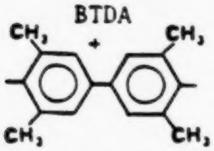
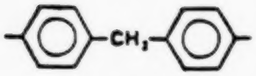
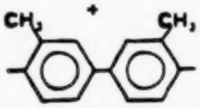
Sorbent	Maximum μV/sec (°C)	Plateau to °C	Peaks Retention Volume (mL), μV
BTDA +  PI-211	0.35(275)	210	NP
PMDA +  PI-131	0.77(271)	242	NP

Table B5. VOLATILE BACKGROUND OF SORBENTS CONTAINING SULFUR

Sorbent	Stability Measurements		
	Maximum μV/sec (°C)	Plateau to °C	Peaks Retention Volume (mL), μV
PMDA +  PI-112	7.0(261)	207	NP
BTDA +  PI-212	0.42(268)	250	NP
PMDA +  PI-116	4.7(275)	230	NP
PMDA +  PI-119	0.25(266)	234	NP
BTDA +  PI-210	0.46(275)	170	NP
PMDA +  PI-125	7.0(261)	211	NP
BTDA +  PI-209	0.45(275)	210	NP
BTDA +  PI-217	0.43(275)	250	NP

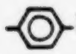
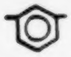
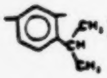
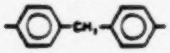
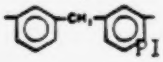
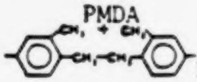
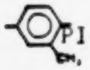
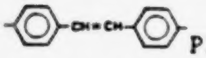
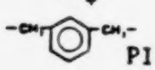
[a] NP = no peaks.

Table B6. VOLATILE BACKGROUND OF SORBENTS WITHOUT HETEROATOMS

Sorbent	Maximum µV/sec (°C)	Plateau to °C	Peaks Retention Volumes (mL), µV
PMDA +  PI-105	8.9(275)	160	NP
PMDA +  PI-109	0.20(270)	250	NP
PMDA +  PI-128	2.2(275)	250	NP
BTDA +  PI-203	0.17(275)	250	NP
PMDA +  PI-1001	0.25(270)	242	NP
PMDA +  PI-1002	0.28(266)	192	NP

continued

Table B6 (Cont'd.)

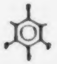
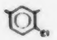
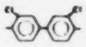
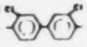
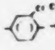
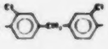
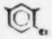
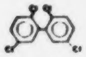
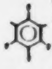
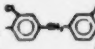
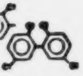
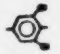
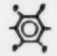
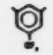
	Stability Measurements		
Sorbent	Maximum µV/sec (°C)	Plateau to °C	Peaks Retention Volume (mL)µV
PMDA +  PI-143	0.52(275)	210	NP
PMDA +  PI-144	0.45(275)	250	NP
PMDA +  PI-147	5.9(275)	202	NP
PMDA +  PI-149	0.83(275)	250	NP
PMDA +  PI-150	0.52(268)	226	NP
PMDA +  PI-142	0.40(275)	240	NP
Tenax-Column 1	0.52(250)	170	NP
Tenax-Column 2	0.33(270)	242	NP
PMDA +  PI-152	2.6(275)	146	NP
PMDA +  PI-153	1.2(250)	138	NP
PMDA +  PI-155	55(275)	122	offscale

APPENDIX C

RETENTION VOLUMES OF TEST SUBSTANCES ON POLYIMIDE SORBENTS

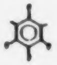
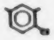
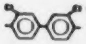
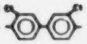
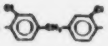
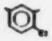
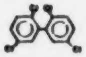
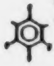
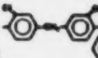
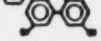
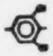
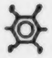
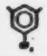
(LEVEL I DATA)

Table C1. RETENTION VOLUMES (mL) OF TEST SUBSTANCES ON THE SORBENTS FROM DIAMINES CONTAINING HALOGENS

			Sorbents														
			PMDA	PMDA	PMDA	BTDA	PMDA	PMDA	BTDA		PMDA	PMDA	BTDA	BTDA	PMDA	PMDA	PMDA
																	
Test substances	Injection size (µL)	Tenax[c]	PI-101	PI-103	PI-121	PI-213	PI-124	PI-108	PI-201	Chromosorb 101	PI-113	PI-116	PI-205	PI-206	PI-115	PI-118	PI-126
C7	5	270		268	120	45	170	390	5	320	88	180	3	3	NP	260	380
	50	270	130	205	110	25	160		5	310	45	18	3	NS	490	220	370
C8	5	320			170	88	230		5	380	140	NS	15			NS	420
	50	320	NS	NS	170	65	220	NS	5	360	95	5	5	NS	NS		390
C9	5	360			220	130	280		15	420	190	NS	45			NS	460
	50	360	NS	NS	220	120	270	NS	15	420	160	93	20	NS	NS	NS	460
C10	5	400			270	170	320		43	460	230	NS	88				490
	50	402	NS	NS	270	160	320	NS	43	460	200	140	53	NS	NS		NS
Benzene	5	230		370	220	63	300	350	5	290	180	270	3	3	380	290	420
	50	230	220	380	220	43	290	370	5	280	120	200	3	3	380	260	420
Ethanol	5	77		270	140	160	220	280	50	140	190	210	85		270	230	320
	50	77	140	280	130	160	210	270	18	140	160	190	85	a	260	220	320
Methyl ethyl ketone	5	190		380	220	250	310	NP	20	250	240	260	90	3	380	320	440
	50	210	270	400	220	250	300	360	18	290	270	260	90		380	NP	440
Nitromethane	5	160		400	140	290	320	NP	NP	210	300	440	300		370	NP	440
	50	160	130	400	130	290	320	430	NP	210	300	420	290	a	370	340	440
Pyridine	5	280		430	360	360	460	NP	180	360	440	390	210		510	450	NP
	50	300	130	430	360	360	460	530	180	360	400	410	210	b	490	430	540

(continued)

Table C1 (Cont'd.)

		Sorbents															
			PMDA	PMDA	PMDA	BTDA	PMDA	PMDA	BTDA		PMDA	PMDA	BTDA	BTDA	PMDA	PMDA	PMDA
																	
Test substances	Injection size (μL)	Tenax[c]	PI-101	PI-103	PI-121	PI-213	PI-124	PI-108	PI-201	Chromosorb 101	PI-113	PI-114	PI-205	PI-206	PI-115	PI-118	PI-126
Acetonitrile	5	110		380	200	260	290	370	250	220	280	390	260		340	310	410
	50	120	390	360	210	250	280	380	240	220	280	390	260	3	340	310	420
Dichloroethane	5	220		390	210	270	290	NP	15	280	220	NP	100		380	270	410
	50	200	140	380	210	250	290	400	5	300	220	230	100	[a]	380	280	410
Vinyl chloride	1 mL	49		13	40	73	100	150	5	75	50	36	3	[a]	180	48	150
Water[b]	50 μL	25	87	37	10	32	18	37	28	5	33	103	10	3	70	40	47

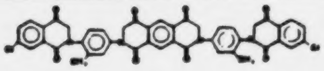
[a] Due to poor retention volumes, these compounds were not tested.

[b] Retention volumes for water were determined at 120°C isothermally.

NP = no peaks.

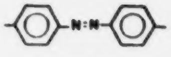
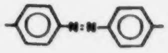
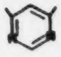
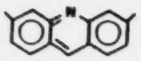
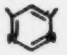
NS = not separated.

Table C2. RETENTION VOLUMES OF TEST SUBSTANCES ON THE TETRAIMIDE SORBENT

		Sorbent	
Test Substance	Injection Size (μL)	 755	Tenax
C7	5	[a]	270
	50	67	270
C8	5	[a]	320
	50	110	320
C9	5	[a]	360
	50	160	360
C10	5	[a]	404
	50	190	400
Benzene	5	[a]	230
	50	49	240
Ethanol	5	[a]	77
	50	25	77
Methyl Ethyl Ketone	5	[a]	200
	50	59	210
Nitromethane	5	[a]	160
	50	78	160
Pyridine	5	[a]	280
	50	180	300
Acetonitrile	5	[a]	110
	50	51	120
Dichloroethane	5	[a]	220
	50	82	200
Vinyl Chloride	1 mL	6	49

[a] Not analyzed.

Table C3. RETENTION VOLUMES AND PEAK SHAPES[a] OF TEST SUBSTANCES ON SORBENTS CONTAINING NITROGEN

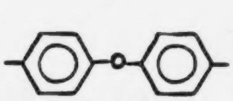
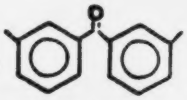
Test substance	Injection size (μL)	Tenax	PMDA +  PI-106	BTDA +  PI-204	PMDA +  PI-130	PMDA +  PI-132	BTDA +  PI-218
C7	5	$270^{sh,sy}$	$300^{b,a}$	$8^{sh,a}$	$330^{sh,sy}$	$180^{b,a}$	$60^{b,sy}$
	50	270	300	3	180	170	45
C8	5	320	NS^{c}	28	NS	230	105
	50	320		18	230	220	90
C9	5	360	NS	65	NS	280	160
	50	360		43	280	280	140
C10	5	400	NS	110	NS	330	200
	50	400		88	330	320	190
Benzene	5	230	$300^{b,a}$	3	$300^{b,sy}$	$420^{b,a}$	$85^{b,a}$
	50	230	300	3	310	420	50
Ethanol	5	77	290	3	$270^{b,a}$	$380^{b,sy}$	130
	50	77	290	3	260	370	120
Methyl Ethyl Ketone	5	200	370	13	$330^{b,sy}$	470	120
	50	200	380	5	320	450	83
Nitromethane	5	160	$380^{b,a}$	$100^{sh,a}$	$370^{b,a}$	$460^{sh,sy}$	280
	50	160	370	100	360	440	280
Pyridine	5	280	$580^{b,a}$	63	450	$550^{b,sy}$	250
	50	300	570	50	440	560	240
Acetonitrile	5	110	330	90	360	$420^{sh,sy}$	$260^{b,sy}$
	50	120	320	68	360	410	250
Dichloroethane	5	220	320	8	320	$410^{b,a}$	$110^{b,a}$
	50	200	310	3	310	410	98
Vinyl Chloride	1mL	49	85	63	120	200	15
Water[b]	50	2.5	$33^{b,a}$	$35^{b,a}$	$140^{b,a}$	$160^{b,a}$	$40^{b,a}$

[a] Code for peak shapes: a = asymmetric, b = broad, sh = sharp, sy = symmetric.

[b] Water retentions done at 120°C.

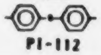
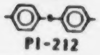
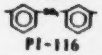
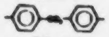
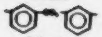
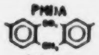
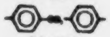
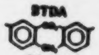
[c] NS = not separated.

Table C4. RETENTION VOLUMES AND PEAK SHAPES OF THE TEST SUBSTANCES ON SORBENTS CONTAINING OXYGEN

Test substances	Injection size (μL)	Tenax	BTDA +  PI-211	PMDA +  PI-131
C7	5	$270^{sh,sy}$	$10^{sh,a}$	$30^{b,a}$
	50	270	5	13
C8	5	320	25	68
	50	318	10	40
C9	5	360	53	100
	50	360	35	85
C10	5	400	85	140
	50	400	75	120
Benzene	5	230	$5^{sh,a}$	38
	50	240	5	18
Ethanol	5	77	85	NP
	50	77	85	$150^{b,sy}$
Methyl Ethyl Ketone	5	200	NP	NP
	50	200	120	160
Nitromethane	5	160	NP	NP
	50	160	$360^{b,a}$	$300^{b,a}$
Pyridine	5	280	230	350
	50	300	240	$340^{b,a}$
Acetonitrile	5	110	320	NP
	50	120	320	260
Dichloroethane	5	220	NP	160
	50	200	$120^{b,a}$	160
Vinyl Chloride	1mL	49	$2.5^{sh,a}$	10
Water	50	2.5	$32^{b,a}$	$55^{b,a}$

[a] sh = sharp, b = broad, sy = symmetrical

Table C5. RETENTION VOLUME AND PEAK SHAPES[a] OF TEST SUBSTANCES FOR THE SORBENTS FROM DIAMINES CONTAINING SULFUR

Test substances	Injection size (µL)	Sorbents								
		PMDA  PI-112	BTDA  PI-212	PMDA  PI-116	PMDA  PI-119	BTDA  PI-210	PMDA  PI-125	BTDA  PI-209	BTDA  PI-217	Tenax[c]
C7	5	360		103	310		110	20	33	270
	50	370sh,sy	3	98	300	3	120	13	28	270
C8	5	220		150	390		180	53	70	320
	50	420	8	140	380	5	160	33	65	320
C9	5	460		200	430		200	95	110	360
	50	460	25	190	430	25	250	78	110	360
C10	5	490		240	470		250	140	160	400
	50	490	65	240	470	65		130	160	400
Benzene	5	390		280	350		NP	48	48	230
	50	390	3	280	340	3	NP	38	15	240
Ethanol	5	280		220	300		280	180	150	77
	50	280	25	210	300	3	280	140	140	77
Methyl ethyl ketone	5	390		320	370		300	210	100	200
	50	380	8	310	370	5	320	220	100	210
Nitromethane	5	370		340			460	310	NP	160
	50	370		340	640	178	460	310	260	160
Pyridine	5	500	225	400	500	10	650	360	340	280
	50	490		400			620	360	330	300
Acetonitrile	5	340	190	300	320		NP	260	280	110
	50	330		300	310	165	NP	260	270	120
Dichloroethane	5	390	200	300	350	5	300	240	90	220
	50	390	3	300	350		300	240	63	200
Vinyl chloride	1 mL	170	3	100	130	3	120	25	13	49
Water[b]	50	33		25	15		78	12	48	2.5

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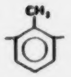
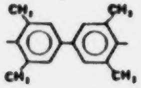
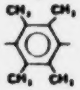
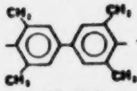
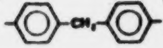
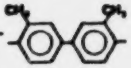
[a] Code for peak shape: sh = sharp; sy = symmetrical.

[b] The retention volume for water was done at 120¼C.

Table C6. RETENTION VOLUMES AND PEAK SHAPES[a] OF TEST SUBSTANCES ON SORBENTS FROM THE DIAMINES WITHOUT HETEROATOMS

Test substance	Injection size (μL)	Tenax	PMDA +  PI-105	PMDA +  PI-109	PMDA +  PI-128	BTDA +  PI-203	PMDA +  PI-1001	PMDA +  PI-1002
C7	5	$270^{sh,sy}$	NP[c]	$430^{sh,sy}$	$590^{b,a}$	$375^{b,a}$	$420^{b,a}$	$35^{b,a}$
	50	270	$390^{b,a}$	430	520	330	400	15
C8	5	320	NS[d]	490	NS	NS	NS	75
	50	320		490				48
C9	5	360	NS	540	NS	NS	NS	120
	50	360		540	NS			100
C10	5	400	NS	590		NS	NS	180
	50	400		590	NS			200
Benzene	5	230	$480^{b,sy}$	450	$480^{b,sy}$	$340^{b,a}$	$420^{b,sy}$	33
	50	240	470	440	480	340	420	28
Ethanol	5	77	380	$330^{sh,a}$	$380^{b,a}$	$320^{b,a}$	$300^{b,a}$	200
	50	77	370	320	380	320	290	200
Methyl Ethyl Ketone	5	200	500	$450^{sh,sy}$	$500^{b,sy}$	$420^{b,a}$	$410^{b,a}$	NP
	50	210	500	450	500	420	410	100
Nitromethane	5	160	$520^{sh,sy}$	430	$500^{sh,sy}$	$440^{b,a}$	$420^{b,a}$	360
	50	160	520	430	500	440	420	360
Pyridine	5	280	600	$560^{sh,a}$	$600^{b,a}$	$540^{b,a}$	$520^{b,a}$	480
	50	300	600	560	610	520	520	460
Acetonitrile	5	110	480	$380^{sh,sy}$	$460^{sh,sy}$	$400^{b,sy}$	$380^{b,sy}$	330
	50	120	470	370	450	380	380	320
Dichloroethane	5	220	$500^{b,sy}$	450	$500^{b,sy}$	$430^{b,a}$	$430^{b,a}$	140
	50	200	500	490	500	430	430	140
Vinyl Chloride	1mL	49	260	210	$250^{sh,sy}$	$200^{b,a}$	$190^{b,a}$	2.5
Water[b]	50	2.5	110	$36^{b,sy}$	$90^{b,a}$	$38^{sh,sy}$	$33^{b,sy}$	$2.5^{sh,sy}$

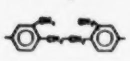
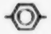
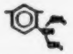
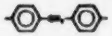
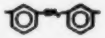
[a] Code for peak shapes: a = asymmetric, b = broad, sy = symmetric, sh = sharp.

[b] Water retention volumes - 120°C.

[c] NP = No peak.

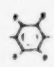
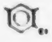
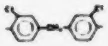
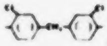
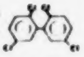
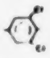
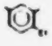
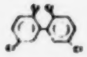
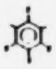
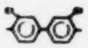
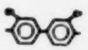
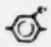
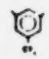
[d] NS = Not separated.

Table C6 (Cont'd.)

Test Substance	Injection Size (µL)	PMDA  PI-142	PMDA  PI-143	PMDA PI-144	PMDA  PI-147	PMDA  PI-149	PMDA  PI-150	Tenax
		Sorbents						
C7	5	$83^{b,a}$	$350^{b,a}$	$392^{b,a}$	$340^{sh,sy}$	$300^{b,a}$	ND	270
	50	50	340	330	340	300	$8^{b,sy}$	270
C8	5	140	390	NS	380	NS	ND	320
	50	103	400		380		26	320
C9	5	200	430	NS	420	NS	ND	360
	50	160	430		410		54	360
C10	5	240	480	NS	450	NS	ND	400
	50	220	NS		450		90	400
Benzene	5	$73^{b,a}$	$360^{b,sy}$	$340^{b,sy}$	360	$300^{b,sy}$	ND	230
	50	33	360	340	360	300	$8^{sh,a}$	240
Ethanol	5	$100^{b,a}$	$290^{b,a}$	$280^{b,a}$	370	210	ND	77
	50	63	280	280	260	210	$70^{b,a}$	77
Methyl Ethyl Ketone	5	$150^{b,a}$	$390^{b,sy}$	$370^{sh,sy}$	360	300	ND	200
	50	140	380	370	360	300	80	210
Nitromethane	5	$260^{b,a}$	$380^{b,sy}$	$360^{sh,sy}$	360	300	ND	160
	50	260	370	360	360	290	203	160
Pyridine	5	$340^{b,a}$	$540^{b,a}$	$490^{sh,a}$	460	$390^{b,a}$	ND	260
	50	340	$550^{sh,a}$	510	460	380	230	300
Acetonitrile	5	$210^{b,a}$	$360^{b,sy}$	$340^{sh,sy}$	330	$260^{b,sy}$	ND	110
	50	210	350	330	330	260	180	120
Dichloroethane	5	ND	$370^{b,sy}$	$390^{b,sy}$	390	310	ND	220
	50	$210^{b,a}$	360	390	380	300	60	200
Vinyl Chloride	1 mL	$5^{sh,a}$	$160^{b,sy}$	$150^{b,sy}$	180	$120^{b,a}$	$2^{sh,a}$	49
Water	50	10	1.3	86	75	18	ND	2.5

[a] Codes for peak shapes: a = asymmetric; b = broad, sh = sharp, sy = symmetric, NS - not separated, ND - not done because low retention volumes were observed.

Table C7. THEORETICAL PLATES FOR TEST SUBSTANCES ON SORBENTS CONTAINING HALOGENS

Test substances	Injection size (µL)	Sorbents														
		PMDA	PMDA	PMDA		BTDA	BTDA	PMDA		BTDA		PMDA	PMDA	BTDA	PMDA	PMDA
																
		PI-118	PI-103	PI-108	Tenax	PI-205	PI-206	PI-115	Chromosorb 101	PI-201	PI-113	PI-114	PI-121	PI-213	PI-124	PI-126
C7	5	13	9	11	1,190	18	0	NP	1,320	64	49	4	73	20	157	625
	50	7	4	8	1,180	16	0	44	1,260	64	13	0	64	8	108	617
C8	5	NS	NS	NS	1,710	NS	NS	NS	2,470	64	125	4	173	68	331	1,760
	50	NS			1,520	NS	NS	NS	2,370	64	34	0	148	27	281	1,060
C9	5	NS	NS	NS	2,180	NS	NS	NS	4,570	36	352	4	359	169	546	1,870
	50	NS			2,300	NS	NS	NS	4,520	36	159	1	281	104	475	2,090
C10	5	NS	NS	NS	2,610	NS	NS	NS	4,530	18	230	4	65	46	134	690
	50	NS			2,800	NS	NS	NS	4,530	18	1,080	2	75	42	138	NS
Benzene	5	22	57	16	526	0	0	163	2,190	0	4	12	16	1	40	259
	50	28	21	10	468	0	0	161	2,080	0	5	2	12	0	25	289
Ethanol	5	21	34	38	101	2		69	210	1	10	7	12	7	34	131
	50	10	12	17	106	1	0	153	210	0	5	3	7	3	33	94
Methyl ethyl ketone	5	50	104	NP	1,550	2		289	2,500	0	10	11	20	14	63	262
	50	49	105	76	586	1		352	2,500	0	8	6	52	7	60	351
Nitromethane	5	NP	310	NP	390	64		301	3,140	NP	135	32	50	62	667	203
	50	45	14,600	32	518	33	0	270	3,140	NP	48	23	26	29	230	92
Pyridine	5	78	189	NP	1,220	4		549	1,300	3	39	30	117	31	270	NP
	50	52	15	165	1,310	4	0	388	1,010	3	24	18	135	13	339	353
Acetonitrile	5	46	324	140	716	24		2,916	3,290	12	56	21	40	24	270	316
	50	27	1,460	140	494	14		8,464	650	6	30	18	49	14	342	660
Dichloroethane	5	42	173	NP	1,860	3		144	1,940	0	10	NP	20	15	48	172
	50	20	40,100	140	840	1		361	6,400	0	7	6	19	10	57	247
Vinyl Chloride	1 mL	2	0	12	118	0	0	36	900	0	1	1	1	1	10	35

APPENDIX D

THEORETICAL PLATE NUMBER FOR TEST SUBTANCES ON POLYIMIDE SORBENTS

(LEVEL I DATA)

Table D1. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON TETRAIMIDE SORBENT

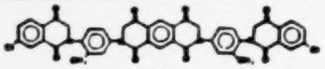
Test Substance	Injection Size	 755	Tenax
C7	5	ND	938
	50	46	939
C8	5	ND	1,360
	50	87	1,250
C9	5	ND	1,780
	50	277	1,970
C10	5	ND	2,420
	50	96	2,580
Benzene	5	ND	714
	50	2	557
Ethanol	5	ND	94
	50	1	90
Methyl Ethyl Ketone	5	ND	1,460
	50	4	749
Nitromethane	5	ND	641
	50	12	518
Pyridine	5	ND	1,010
	50	14	1,050
Acetonitrile	5	ND	805
	50	4	452
Dichloroethane	5	ND	1,680
	50	13	771
Vinyl Chloride	1 mL	1	88

Table D2. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON SORBENTS CONTAINING NITROGEN

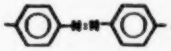
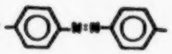
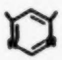
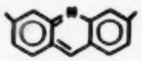
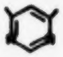
Test substance	Injection size (μL)	Tenax	PMDA +  PI-106	BTDA +  PI-204	PMDA +  PI-130	PMDA +  PI-132	 PI-218
C7	5	938	8	4	180	207	28
	50	939	8	1	193	125	20
C8	5	1,365	NS	8	NS	339	87
	50	1,248		22	346	262	52
C9	5	1,785	NS	42	NS	502	206
	50	1,967		14	511	484	125
C10	5	2,418	NS	23	NS	130	444
	50	2,575		10	356	140	361
Benzene	5	714	24	0	62	55	5
	50	557	27	0	156	38	1
Ethanol	5	94	33	0	80	400	4
	50	90	40	0	41	447	2
Methyl Ethyl Ketone	5	1,462	90	1	110	180	5
	50	749	42	0	107	119	1
Nitromethane	5	641	400	2	166	3,680	58
	50	518	87	2	59	1,714	31
Pyridine	5	1,007	60	1	297	860	28
	50	1,047	102	0	116	342	11
Acetonitrile	5	805	92	2	114	2,277	32
	50	452	52	1	171	1,076	25
Dichloroethane	5	1,684	46	0	97	187	4
	50	771	22	0	65	201	2
Vinyl Chloride	1mL	88	4	4	17	67	0

Table D3. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON SORBENTS CONTAINING OXYGEN

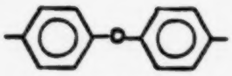
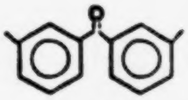
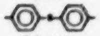
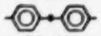
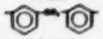
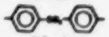
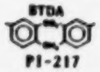
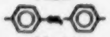
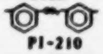
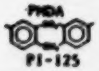
Test substances	Injection size (μL)	Tenax	BTDA +  PI-211	PMDA +  PI-131
C7	5	938	10	12
	50	939	4	4
C8	5	1,360	16	60
	50	1,250	4	18
C9	5	1,780	36	137
	50	1,970	12	72
C10	5	2,420	46	189
	50	2,580	30	47
Benzene	5	714	0	1
	50	557	0	0
Ethanol	5	94	3	NP
	50	90	1	4
Methyl Ethyl Ketone	5	1,460	NP	NP
	50	749	8	3
Nitromethane	5	641	NP	NP
	50	518	23	47
Pyridine	5	1,010	4	28
	50	1,050	4	13
Acetonitrile	5	805	32	NP
	50	452	17	34
Dichloroethane	5	1,680	NP	6
	50	771	3	3
Vinyl Chloride	1mL	88	0	0

Table D4. THEORETICAL PLATE NUMBER FOR TEST SUBSTANCES ON SORBENTS CONTAINING SULFUR

Test substances	Injection size (µL)	Sorbents								
		PMDA  PI-112	BTDA  PI-212	PMDA  PI-116	BTDA  PI-209	BTDA  PI-217	PMDA  PI-119	BTDA  PI-210	PMDA  PI-125	Tenax
C7	5	645		83	7	14	605		74	1,190
	50	553	16	75	6	10	492	4	114	1,180
C8	5	1,100		184	28	42	1,060		249	1,710
	50	1,360	144	149	7	27	936	4	174	1,520
C9	5	2,380		390	71	112	1,460		419	2,180
	50	1,850	8	293	38	100	1,440	7	332	2,300
C10	5	690		198	56	127	1,160		49	2,610
	50	1,570	27	164	48	455	1,730	30	25	2,800
Benzene	5	1,330		14	1	0	1,600		NP	526
	50	1,500	0	11	0	0	718	0	NP	468
Ethanol	5	1,420		60	11	9	900		21	101
	50	988	0	32	7	5	1,160	0	16	106
Methyl ethyl ketone	5	1,500		71	12	2	2,400		49	1,550
	50	2,640	0	52	5	2	3,460	0	40	586
Nitromethane	5	5,550		425	56	NP	9,220		65	390
	50	4,330	8	366	116	15	3,140	6	99	518
Pyridine	5	1,310		196	27	17	107		62	1,220
	50	776	2	127	27	23	33	0	39	1,330
Acetonitrile	5	1,470		265	64	10	2,580		NP	716
	50	1,440	4	109	100	9	1,710	3	NP	494
Dichloroethane	5	6,010		62	12	1	3,140		31	1,840
	50	1,960	0	41	10	1	2,180	0	24	840
Vinyl chloride	1 mL	366	0	20	1	0	416	0	5	118

NP = no peak.

Table D5. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON SORBENTS FROM DIAMINES WITHOUT HETEROATOMS

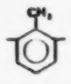
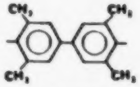
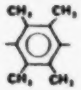
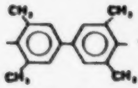
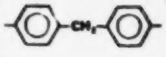
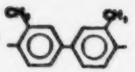
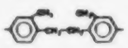
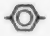
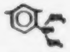
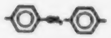
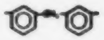
Test substances	Injection size (μL)	PMDA +  PI-105	PMDA +  PI-109	PMDA +  PI-128	Tenax	BTDA +  PI-203	PMDA +  PI-1001	PMDA +  PI-1002
C7	5	NP	3,320	105	938	31	30	10
	50	18	1,890	67	939	11	28	4
C8	5	NS	4,270	NS	1,360	NS	NS	36
	50		2,430		1,250			18
C9	5	NS	5,180	NS	1,780	NS	NS	100
	50		3,880		1,970			41
C10	5	NS	6,140	NS	2,420	NS	NS	52
	50		6,240		2,580			28
Benzene	5	270	5,130	1,220	714	18	282	0
	50	159	1,940	873	557	15	167	0
Ethanol	5	699	1,400	936	94	25	199	8
	50	447	1,200	1,130	90	36	102	5
Methyl Ethyl Ketone	5	396	5,130	2,500	1,460	68	425	NP
	50	381	5,130	1,620	749	35	420	1
Nitromethane	5	4,807	7,400	4,440	641	429	1,810	213
	50	4,057	3,250	3,200	518	378	1,760	95
Pyridine	5	915	1,190	1,600	1,010	114	1,430	40
	50	699	1,630	824	1,050	87	272	16
Acetonitrile	5	642	1,890	5,360	805	277	405	73
	50	2,233	1,560	3,640	452	215	459	32
Dichloroethane	5	331	3,600	2,520	1,680	102	967	2
	50	334	4,220	2,000	771	47	462	1
Vinyl Chloride	1mL	212	1,100	1,090	88	25	58	0

Table D5. (Cont'd.)

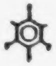
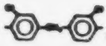
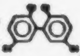
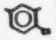
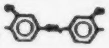
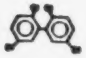
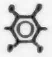
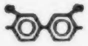
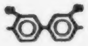
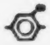
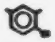
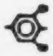
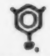
Test Substance	Injection Size (μL)	Sorbents						
		PMDA  PI-142	PMDA  PI-143	PMDA PI-144	PMDA  PI-147	PMDA  PI-149	PMDA  PI-150	Tenax
C7	5	33	802	34	4,733	46		938
	50	20	424	33	3,250	44	4	939
C8	5	111	1,300	NS	6,022	NS		1,360
	50	47	1,320		4,100		14	1,250
C9	5	337	1,920	NS	7,190	NS		1,780
	50	121	201		4,950		3	1,970
C10	5	141	908	NS	5,780	NS		2,420
	50	51	NS		8,240		32	2,580
Benzene	5	1	518	851	5,300	633		714
	50	0	506	339	5,240	576	0	557
Ethanol	5	3	303	121	3,000	378		94
	50	1	188	108	1,440	883	4	90
Methyl Ethyl Ketone	5	5	1,200	392	5,360	1,420		1,460
	50	3	288	267	8,280	1,110	2	749
Nitromethane	5	120	1,480	2,800	3,800	1,080		641
	50	86	1,760	1,320	8,370	3,460	38	518
Pyridine	5	82	380	364	2,210	1,510		1,010
	50	93	386	462	957	2,950	15	1,050
Acetonitrile	5	71	1,420	3,250	7,140	4,220		805
	50	41	1,530	1,140	7,060	1,380	7	452
Dichloroethane	5	NP	1,360	2,400	9,600	1,460		1,680
	50	9	443	1,270	4,220	924	1	771
Vinyl Chloride	1 mL	0	50	243	1,350	576	0	88

APPENDIX E

ELUTION TEMPERATURES OF TEST SUBSTANCES ON POLYIMIDE SORBENTS

(LEVEL I DATA)

Table E1. ELUTION TEMPERATURES OF TEST SUBSTANCES ON SORBENTS CONTAINING HALOGENS

Test substances	Injection size (µL)	Sorbents														
		PMDA  PI-114	BTDA  PI-205	 PI-206	Chromosorb 101	BTDA  PI-201	PMDA  PI-108	PMDA  PI-113	PMDA  PI-118	PMDA  PI-121	BTDA  PI-213	PMDA  PI-126	Tenax	PMDA  PI-103	PMDA  PI-115	PMDA  PI-126
C7	5	108	62	51	152	52	174	78	135	88	64	105	141	136	NP	170
	50	56	58	51	152	52	156	64	122	85	58	102	136	116	207	169
C8	5	108	62	NS	169	52	NS	95	NS	105	78	123	157	NS	NS	184
	50	66	58	NS	169	52	NS	80	NS	104	70	120	153			176
C9	5	108	62	NS	185	55	NS	110	NS	122	92	139	172	NS	NS	197
	50	79	58	NS	185	55	NS	100	NS	120	87	137	167			196
C10	5	108	62	NS	198	64	NS	123	NS	137	104	154	184	NS	NS	208
	50	95	58	NS	198	64	NS	116	NS	136	102	153	180			NS
Benzene	5	135	51	51	144	52	162	106	142	121	70	146	122	167	172	185
	50	112	51	51	141	52	168	90	135	120	64	144	123	171	172	186
Ethanol	5	116	77		96	66	139	111	123	96	103	120	74	136	136	151
	50	110	77	51	96	56	137	101	120	93	102	119	74	141	134	151
Methyl ethyl ketone	5	134	79		130	56	NP	127	152	122	132	148	109	172	172	192
	50	132	79		130	56	164^a	136	153	122	130	146	115	177	170	192
Nitromethane	5	186	146		117	NP	NP	148	NP	94	144	153	101	177	168	192
	50	181	143	55	117	NP	189^a	147	160	93	144	153	100	177	168	192
Pyridine	5	170	119		165	106	NP	189	195	167	165	198	138	187	214	NP
	50	178	119	51	164	106	220^a	178	188	166	165	197	140	135	208	223
Acetonitrile	5	170	132		119	130	171	140	150	116	135	142	86	172	158	182
	50	173	133		121	126	171	138	148	117	132	139	86	166	160	184
Dichloroethane	5	NP	82		138	55	NP	120	138	116	138	144	118	171	170	181
	50	122	82		146	52	178^a	122	140	117	131	144	119	176	172	182
Vinyl chloride	1 mL	61	51	51	74	52	98	66	65	63	73	82	65	54	106	97

[a] <5% response at low attenuations.

Table E2. ELUTION TEMPERATURES OF TEST SUBSTANCES ON TETRAIMIDE SORBENT

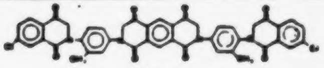
Test Substance	Injection Size	 755	Tenax
C7	5	ND	138
	50	77	136
C8	5	ND	154
	50	95	153
C9	5	ND	168
	50	113	167
C10	5	ND	181
	50	128	180
Benzene	5	ND	124
	50	70	125
Ethanol	5	ND	75
	50	60	75
Methyl Ethyl Ketone	5	ND	112
	50	74	116
Nitromethane	5	ND	102
	50	82	103
Pyridine	5	ND	140
	50	125	145
Acetonitrile	5	ND	87
	50	71	88
Dichloroethane	5	ND	120
	50	84	121
Vinyl Chloride	1 mL	52	65

Table E3. ELUTION TEMERATURES OF TEST SUBSTANCES ON SORBENTS CONTAINING NITROGEN

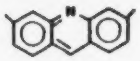
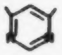
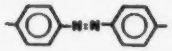
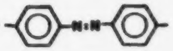
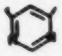
Test substance	Injection size (μL)	Tenax	PMDA +  PI-132	BTDA +  PI-218	PMDA +  PI-106	BTDA +  PI-204	PMDA +  PI-130
C7	5	138	108	69	146	52	157
	50	136	104	64	146	51	108
C8	5	154	124	84	NS	59	NS
	50	153	121	79		57	124
C9	5	168	140	99	NS	71	NS
	50	167	138	95		64	140
C10	5	181	155	113	NS	84	NS
	50	180	154	111		78	156
Benzene	5	124	186	77	148	51	148
	50	125	186	66	147	51	150
Ethanol	5	75	170	92	142	51	136
	50	75	168	88	141	51	132
Methyl Ethyl Ketone	5	112	200	88	168	54	155
	50	116	194	76	172	52	153
Nitromethane	5	102	196	141	170	84	168
	50	103	191	140	169	84	167
Pyridine	5	140	226	130	236	70	195
	50	147	228	127	232	66	192
Acetonitrile	5	87	184	132	148	79	165
	50	88	181	130	156	72	165
Dichloroethane	5	120	181	84	151	52	152
	50	121	180	81	148	51	150
Vinyl Chloride	1mL	65	116	55	77	70	88

Table E4. ELUTION TEMPERATURES OF TEST SUBSTANCES ON SORBENTS CONTAINING OXYGEN

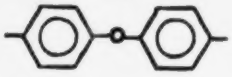
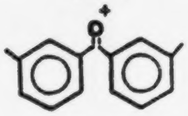
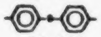
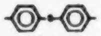
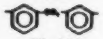
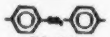
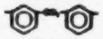
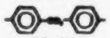
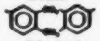
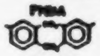
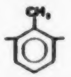
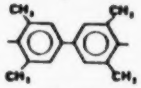
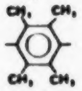
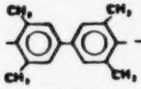
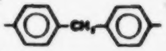
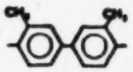
Test substances	Injection size (μL)	Tenax	PMDA +  PI-211	BTDA +  PI-131
C7	5	138	53	60
	50	136	52	54
C8	5	154	58	72
	50	153	53	63
C9	5	168	67	83
	50	167	61	77
C10	5	181	77	94
	50	180	74	88
Benzene	5	124	52	62
	50	125	52	56
Ethanol	5	75	77	NP
	50	75	77	98
Methyl Ethyl Ketone	5	112	NP	NP
	50	116	90	101
Nitromethane	5	102	NP	NP
	50	103	165	146
Pyridine	5	140	124	162
	50	147	128	159
Acetonitrile	5	87	154	NP
	50	88	152	132
Dichloroethane	5	120	NP	103
	50	121	90	100
Vinyl Chloride	1mL	65	51	53

Table E5. ELUTION TEMPERATURES OF TEST SUBSTANCES ON SORBENTS CONTAINING SULFUR

Test substances	Injection size (µL)	Sorbents								T_{max}^{c}
		PMDA  PI-112	BTDA  PI-212	PMDA  PI-116	PMDA  PI-119	BTDA  PI-210	BTDA  PI-209	BTDA  PI-217	PMDA  PI-125	
C7	5	167		83	148		56	60	84	141
	50	168	51	81	148	51	54	59	88	136
C8	5	183		99	174		67	72	107	157
	50	183	52	96	172	52	60	71	103	153
C9	5	196		113	188		80	86	120	172
	50	196	58	112	187	58	75	86	116	167
C10	5	208		126	200		95	100	131	184
	50	208	71	127	200	71	92	101	130	180
Benzene	5	174		140	162		65	65	NP	122
	50	174	51	138	157	51	62	55	NP	123
Ethanol	5	140		121	146		107	98	141	74
	50	138	58	118	145	51	106	96	140	74
Methyl ethyl ketone	5	176		151	168		117	82	148	109
	50	173	52	148	168	52	120	82	154	115
Nitromethane	5	169		157	165		149	NP	196	101
	50	168	122	157	162	107	149	135	197	100
Pyridine	5	209		179	256		165	157	258	138
	50	206	111	176	212	53	164	156	250	140
Acetonitrile	5	157		148	152		135	138	NP	86
	50	156	114	146	149	103	134	136	NP	86
Dichloroethane	5	176		148	162		127	79	146	118
	50	174	51	146	162	52	125	70	146	119
Vinyl chloride	1 mL	104	51	84	91	51	58	54	87	65

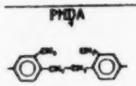
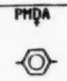
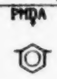
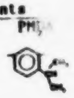
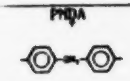
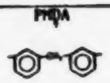
NP = no peak.

Table E6. ELUTION TEMPERATURES OF TEST SUBSTANCES ON SORBENTS FROM DIAMINES WITHOUT HETEROATOMS

Test substances	Injection size (μL)	PMDA +  PI-105	PMDA +  PI-109	PMDA +  PI-128	Tenax	BTDA +  PI-203	PMDA +  PI-1001	PMDA +  PI-1002
C7	5	NP	188	239	138	170	184	61
	50	175	189	216	136	157	178	55
C8	5	NS	207	NS	154	NS	NS	74
	50		208	NS	153			65
C9	5	NS	223	NS	168	NS	NS	90
	50		224	NS	167			82
C10	5	NS	238	NS	181	NS	NS	108
	50		240	NS	180			114
Benzene	5	204	193	204	124	157	184	60
	50	201	191	204	125	157	184	56
Ethanol	5	172	155	172	75	154	146	114
	50	168	154	171	75	153	143	114
Methyl Ethyl Ketone	5	209	193	210	112	186	182	NP
	50	210	193	211	116	183	181	82
Nitromethane	5	216	188	210	102	191	186	167
	50	216	187	208	103	190	184	167
Pyridine	5	244	229	242	140	221	216	202
	50	240	228	245	147	218	215	199
Acetonitrile	5	202	172	196	87	176	171	156
	50	201	168	195	88	173	170	152
Dichloroethane	5	210	194	211	120	188	187	93
	50	211	206	211	121	187	188	93
Vinyl Chloride	1mL	132	116	129	65	112	111	51

(continued)

Table E6 (Cont'd.)

Test Substance	Injection Size (μL)	Sorbents						
		 PI-142	 PI-143	 PI-144	 PI-147	 PI-149	 PI-150	Tenax
C7	5	76	192	211	188	172		138
	50	66	190	186	187	170	53	136
C8	5	96	208	NS	205	NS		154
	50	83	210		204		60	153
C9	5	112	225	NS	220	NS		168
	50	103	226		219		72	167
C10	5	126	243	NS	232	NS		181
	50	121	NS		232		86	180
Benzene	5	73	196	190	196	171		124
	50	60	194	190	195	170	53	125
Ethanol	5	82	168	164	160	136		75
	50	70	165	162	156	133	78	75
Methyl Ethyl Ketone	5	98	209	200	196	171		112
	50	93	206	200	196	170	82	116
Nitromethane	5	133	204	198	198	168		102
	50	132	201	196	196	168	132	103
Pyridine	5	159	268	248	238	205		140
	50	158	274	256	236	202	142	147
Acetonitrile	5	117	193	187	185	154		87
	50	116	191	185	184	154	124	88
Dichloroethane	5	NP	197	207	207	172		120
	50	117	193	207	206	172	74	121
Vinyl Chloride	1 mL	52	112	112	124	98	51	65

APPENDIX F

V_n, V_s AND N FOR TEST SUBSTANCES ON POLYIMIDE SORBENTS

(LEVEL II DATA)

Table F1. NET RETENTION VOLUMES V_n, SPECIFIC RETENTION VOLUME V_s, AND NUMBER OF THEORETICAL PLATES N FOR TEST SUBSTANCES. SAMPLE LIFE DEPENDENCE.

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
Tenax	Acetonitrile	100	1.60	117	4.24	331
		50	3.60	117	4.24	331
		10	4.19	127	4.58	331
		1.0	4.82	136	4.92	331
		0.5	5.15	141	5.09	331
		0.5	5.15	141	5.09	331
	Methyl ethyl ketone	100	0.19	131	4.73	355
		50	0.30	146	5.28	355
		10	0.73	171	6.19	355
		1.0	1.18	181	6.55	355
		0.5	1.25	187	6.74	355
		0.5	1.25	187	6.74	355
	Benzene	100	0.16	147	5.30	365
		50	0.21	154	5.58	365
		10	0.36	182	6.58	365
		1.0	0.41	192	6.95	365
		0.5	0.43	197	7.13	365
		0.5	0.42	195	7.04	365
	Pyridine	200	0.51	125	4.51	387
		100	1.42	125	4.51	387
		50	1.54	130	4.70	387
		10	1.79	141	5.08	387
		1.0	1.93	146	5.28	387
		0.5	1.86	143	5.18	387
		0.5	1.86	143	5.18	387
	Dichloroethane	100	0.42	152	5.49	361
		50	0.69	167	6.04	361
		10	1.85	183	6.59	361
		1.0	1.28	190	6.87	361
		0.5	1.28	190	6.87	361
		0.5	2.00	190	6.87	361

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($\times 10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
Tenax	**Octane**	100	0.04	122	4.42	388
		50	0.06	170	6.15	388
		10	0.05	186	6.73	388
		1.0	0.07	197	7.12	388
		0.5	0.06	197	7.12	388
		0.5	0.06	197	7.12	388
	Nitromethane	1000	0.24	202	7.30	333
		100	0.90	271	9.79	333
		50	1.25	283	10.2	333
		10	1.27	285	10.3	333
		1.0	1.35	295	10.7	333
		0.5	1.35	295	10.7	333
		0.5	1.40	300	10.8	333
	Vinyl chloride	0.3	0.81	209	7.54	297
		0.1	0.88	217	7.85	297
		0.1	0.83	211	7.62	297
	Ethanol	900	0.13	284	10.2	298
		100	0.43	399	14.4	298
		50	0.56	437	15.8	298
		10	0.66	474	17.1	298
		1.0	0.75	506	18.3	298
		0.5	0.72	522	18.8	298
		0.5	0.69	511	18.4	298
	Propylene oxide	100	0.15	133	4.79	324
		50	0.30	151	5.47	324
		10	0.57	186	6.73	324
		1.0	0.90	205	7.40	324
		0.5	0.72	210	7.57	324
		0.5	0.73	212	7.65	324

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
Tenax	Acrolein	100	0.21	130	4.68	328
		50	0.32	141	5.11	328
		10	1.28	177	6.39	328
		1.0	1.42	186	6.73	328
		0.5	2.33	191	6.90	328
		0.5	1.45	189	6.81	328
	Pyridine	100	0.76	88.2	1.19	488
		50	0.73	86.3	1.16	488
		10	0.83	92.1	1.24	488
		1.0	0.62	99.7	1.34	488
		0.5	0.62	99.7	1.34	488
		0.5	0.60	97.8	1.31	488
	Dichloroethane	100	0.57	110	1.47	440
		50	0.61	113	1.52	440
		10	0.61	113	1.52	440
		1.0	0.65	117	1.57	440
		0.5	0.65	117	1.57	440
		0.5	0.94	117	1.57	440
	Octane	100	0.16	119	1.60	453
		50	0.18	125	1.68	453
		10	0.19	131	1.76	453
		1.0	0.20	132	1.78	453
		0.5	0.22	138	1.86	453
		0.5	0.19	140	1.88	453
	Nitromethane	100	0.89	133	1.79	428
		50	0.94	137	1.79	428
		10	0.72	140	1.88	428
		1.0	0.55	140	1.88	428
		0.5	0.72	140	1.88	428
		0.5	0.72	140	1.88	428

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
109	Vinyl chloride	0.3	0.52	137	1.84	357
		0.1	0.53	139	1.86	357
		0.1	0.53	139	1.86	357
	Ethanol	900	0.22	179	2.40	383
		100	0.34	236	3.18	383
		50	0.38	252	3.38	383
		10	0.34	277	3.73	383
		1.0	0.38	296	3.98	383
		0.5	0.38	308	4.14	383
		0.5	0.37	318	4.27	383
	Acrolein	100	0.35	136	1.83	405
		50	0.51	148	1.99	405
		20	0.57	157	2.11	405
		1.0	0.53	169	2.27	405
		0.5	0.54	171	2.29	405
		0.5	0.55	172	2.32	405
	Propylene oxide	100	0.30	137	1.84	394
		50	0.36	151	2.03	394
		10	0.37	166	2.24	394
		1.0	0.42	178	2.40	394
		0.5	0.38	182	2.44	394
		0.5	0.48	190	2.56	394
	Benzene	800	0.19	117	1.58	435
		100	0.37	124	1.67	435
		50	0.36	122	1.65	435
		10	0.53	131	1.76	435
		1.0	0.44	134	1.81	435
		0.5	0.55	134	1.81	435
		0.5	0.44	134	1.81	435

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N $(X10^{-3})$	V_N (mL)	V_S (mL/M^2)	Temperature K
109	Methyl ethyl ketone	700	0.18	92.5	1.24	435
		100	0.38	118	1.58	435
		50	0.40	121	1.63	435
		10	0.49	134	1.80	435
		1.0	0.44	143	1.92	435
		0.5	0.48	150	2.02	435
		0.5	0.52	156	2.10	435
	Acetonitrile	700	0.34	109	1.47	414
		100	0.69	136	1.83	414
		50	0.45	125	1.68	414
		10	0.72	139	1.87	414
		1.0	0.60	145	1.94	414
		0.5	0.61	146	1.97	414
		0.5	0.61	146	1.97	414
119	Vinyl chloride	0.3	0.98	72.4	1.83	345
		0.1	0.98	72.4	1.83	345
		0.1	0.98	72.4	1.83	345
	Benzene	1000	0.02	31.4	0.79	375
		100	0.04	273	6.90	375
		10	0.11	593	15	375
		1.0	0.18	787	19.9	375
		0.5	0.19	822	20.8	375
		0.5	0.19	813	20.6	375
	Octane	1000	0.01	10.3	0.26	399
		100	0.01	142	3.60	399
		10	0.02	379	9.59	399
		1.0	0.02	480	12.1	399
		0.5	0.02	474	12	399
		0.5	0.02	490	12.4	399

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
119	Propylene oxide	100	0.05	50.3	1.27	377
		50	0.15	98.6	2.49	377
		10	0.34	135	3.42	377
		1.0	0.29	124	3.13	377
		0.5	0.17	137	3.47	377
		0.5	0.17	137	3.47	377
	Ethanol	100	0.09	38.7	0.98	391
		50	0.63	63.1	1.60	391
		10	0.71	67.2	1.70	391
		1.0	1.03	81.5	2.06	391
		0.5	0.31	89.6	2.27	391
		0.5	0.70	89.6	2.27	391
	Acrolein	100	0.15	70.4	1.78	394
		50	0.22	86.5	2.19	394
		10	0.34	109	2.75	394
		1.0	0.88	125	31.6	394
		0.5	0.94	129	3.26	394
		0.5	0.65	129	3.26	394
	Nitromethane	100	0.68	292	7.38	393
		50	0.84	325	8.21	393
		10	0.89	335	8.47	393
		1.0	0.73	349	8.83	393
		0.5	0.75	353	8.93	393
		0.5	0.67	357	9.03	393
	Acetonitrile	100	0.18	217	5.48	383
		50	0.25	239	6.03	383
		10	0.42	279	7.05	383
		1.0	0.65	323	8.16	383
		0.5	0.71	339	8.57	383
		0.5	0.69	335	8.47	383

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
119	Dichloroethane	100	0.12	146	3.69	403
		50	0.22	167	4.22	403
		10	0.36	200	5.06	403
		1.0	0.41	213	5.38	403
		0.5	0.50	217	5.48	403
		0.5	0.46	225	5.70	403
	Methyl ethyl ketone	100	0.10	97.1	2.46	412
		50	0.13	112	2.83	412
		10	0.35	150	3.79	412
		1.0	0.36	169	4.27	412
		0.5	0.48	175	4.43	412
		0.5	0.72	167	4.22	412
	Pyridine	100	0.03	9.7	0.25	522
		50	0.01	38.8	0.98	522
		10	0.01	38.8	0.98	522
		1.0	0.01	146	3.69	522
		0.5	0.02	216	5.47	522
		0.5	0.01	192	4.85	522
140	Ethanol	1000	0.01	113	1.54	367
		100	0.02	185	2.52	367
		10	0.04	645	8.78	367
		1.0	0.06	816	11.1	367
		0.5	0.08	852	11.6	367
		0.5	0.05	860	11.7	367
	Acetonitrile	1000	0.14	162	2.20	397
		100	0.14	203	2.76	397
		10	0.15	210	2.86	397
		1.0	0.18	225	3.07	397
		0.5	0.18	228	3.10	397
		0.5	0.19	233	3.17	397

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($\times 10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
140	Dichloroethane	1000	0.01	180	2.45	390
		100	0.02	326	4.43	390
		10	0.02	498	6.78	390
		1.0	0.04	493	6.71	390
		0.5	0.05	506	6.88	390
		0.5	0.05	493	6.71	390
	Nitromethane	1000	0.06	184	2.50	392
		100	0.08	345	4.69	392
		10	0.13	458	6.23	392
		1.0	0.19	465	6.33	392
		0.5	0.17	468	6.36	392
		0.5	0.16	468	6.36	392
	Methyl ethyl ketone	1000	0.01	141	1.92	392
		100	0.02	498	6.77	392
		10	0.03	722	9.82	392
		1.0	0.04	817	11.1	392
		0.5	0.03	832	11.3	392
		0.5	0.03	832	11.3	392
	Benzene	1000	0.01	106	1.44	393
		100	0.01	395	5.38	393
		10	0.03	677	9.21	393
		1.0	0.02	743	10.1	393
		0.5	0.03	751	10.2	393
	Vinyl chloride	0.3	0.06	97.1	1.32	354
		0.1	0.05	99.4	1.35	354
		0.1	0.06	102	1.38	354

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
140	Pyridine	1000	0.03	82.8	1.13	440
		100	0.04	195	2.65	440
		10	0.06	355	4.83	440
		1.0	0.06	497	6.76	440
		0.5	0.05	580	7.89	440
		0.5	0.04	558	7.60	440
	Propylene oxide	100	0.02	97.5	1.33	388
		50	0.03	135	1.84	388
		10	0.04	155	2.11	388
		1.0	0.04	163	2.21	388
		0.5	0.04	165	2.25	388
	Acrolein	100	0.07	158	2.15	393
		50	0.05	183	2.49	393
		10	0.12	198	2.70	393
		1.0	0.11	206	2.80	393
		0.5	0.12	216	2.94	393
		0.5	0.12	211	2.87	393
		0.5	0.12	211	2.87	393
149	Propylene oxide	100	0.06	130	-	376
		50	0.06	148	-	376
		10	0.07	165	-	376
		1.0	0.08	179	-	376
		0.5	0.07	181	-	376
		0.05	0.07	181	-	376
	Benzene	800	0.03	116	-	405
		100	0.04	167	-	405
		50	0.04	174	-	405
		10	0.08	197	-	405
		1.0	0.04	204	-	405
		0.5	0.04	206	-	405
		0.5	0.04	202	-	405

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_n (mL)	V_S (mL/M^2)	Temperature K
149	Acetonitrile	700	0.30	98.3	-	396
		100	0.69	126	-	396
		50	1.16	130	-	396
		10	1.37	142	-	396
		1.0	1.42	144	-	396
		0.5	0.99	151	-	396
		0.5	0.99	151	-	396
	Methyl ethyl ketone	700	0.06	124	-	404
		100	0.07	177	-	404
		50	0.08	182	-	404
		10	0.09	208	-	404
		1.0	0.09	217	-	404
		0.5	0.09	219	-	404
		0.5	0.10	222	-	404
	Dichloroethane	1000	0.10	191	-	403
		100	0.10	216	-	403
		50	0.11	230	-	403
		10	0.15	237	-	403
		1.0	0.11	240	-	403
		0.5	0.10	240	-	403
		0.5	0.11	237	-	403
	Octane	620	0.01	68.1	-	414
		100	0.01	117	-	414
		50	0.01	115	-	414
		10	0.01	110	-	414
		1.0	0.01	141	-	414
		0.5	0.01	141	-	414
		0.5	0.01	141	-	414

(continued)

Table F1. (cont'd.)

Sorbent	Compound	Concentration (μg)	N ($X10^{-3}$)	V_N (mL)	V_S (mL/M^2)	Temperature K
149	Ethanol	700	0.10	84.2	-	378
		100	0.17	122	-	378
		50	0.20	131	-	378
		10	0.21	133	-	378
		1.0	0.20	157	-	378
		0.5	0.20	157	-	378
		0.5	0.21	160	-	378
	Pyridine	900	0.26	81.2	-	447
		100	0.40	123	-	447
		50	0.48	135	-	447
		10	0.41	167	-	447
		1.0	0.43	192	-	447
		0.5	0.41	209	-	447
		0.5	0.41	209	-	447
	Acrolein	700	0.12	71.8	-	390
		100	0.30	96.5	-	390
		50	0.38	110	-	390
		10	0.50	126	-	390
		1.0	0.59	137	-	390
		0.5	0.61	139	-	390
		0.5	0.59	137	-	390
	Vinyl chloride	0.3	0.07	202	-	332
		0.1	0.07	202	-	332
		0.1	0.09	202	-	332
	Nitromethane	1000	0.35	89.9	-	409
		100	0.72	129	-	409
		50	1.12	129	-	409
		10	1.16	131	-	409
		1.0	2.37	141	-	409
		0.5	1.37	143	-	409
		0.5	1.37	143	-	409

APPENDIX G

V_n, V_s, AND N FOR TEST SUBSTANCES ON POLYIMIDE SORBENTS - TEMPERATURE DEPENDENCE

(LEVEL II DATA)

Table G1. NET RETENTION VOLUME V_n, SPECIFIC RETENTION VOLUME V_s, AND NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES. TEMPERATURE DEPENDENCE.

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
Tenax	Acetonitrile	267	9.65	2.14	319
		276	9.98	1.68	319
		276	9.98	1.68	319
		203	7.34	2.74	324
		210	7.26	2.68	324
		208	7.51	2.87	324
		136	2.92	4.82	331
		141	5.09	5.15	331
		141	5.09	5.15	331
		88.8	3.21	8.00	340
		88.8	3.21	8.00	340
		88.8	3.21	8.00	340
	Acrolein	326	11.8	1.40	318
		335	12.1	1.20	318
		322	11.6	1.36	318
		186	6.73	1.42	328
		191	6.90	2.33	328
		189	6.81	1.45	328
		101	3.66	10.2	339
		101	3.66	10.2	339
		101	3.66	10.2	339
	Benzene	647	23.4	0.26	345
		654	23.6	0.25	345
		647	23.4	0.26	345
		355	12.8	0.32	355
		355	12.8	0.32	355
		355	12.8	0.32	355
		192	6.95	0.41	365
		197	7.13	0.43	365
		195	7.04	0.42	365
		118	4.28	0.76	375
		118	4.28	0.76	375
		116	4.18	0.73	375
	Dichloroethane	674	24.4	0.82	340
		677	24.4	0.83	340
		674	24.4	0.82	340
		346	12.5	0.91	350
		346	12.5	0.91	350
		353	12.7	0.95	350
		190	6.87	1.28	361
		190	6.87	1.28	361
		190	6.87	2.00	361
		111	4.00	2.68	371
		111	4.00	2.68	371
		111	4.00	2.68	371

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
Tenax	Ethanol	506	18.3	0.75	298
		522	18.8	0.72	298
		511	18.4	0.69	298
		166	6.01	1.90	314
		171	6.17	2.00	314
		178	6.42	1.38	314
		97.6	3.52	10.2	323
		97.6	3.52	10.2	323
		97.6	3.52	10.2	323
	Methyl ethyl ketone	704	25.4	0.70	334
		694	25.1	0.63	334
		689	24.9	0.73	334
		372	13.4	0.89	345
		377	13.6	0.91	345
		372	13.4	0.89	345
		181	6.55	1.18	355
		187	6.74	1.25	355
		187	6.74	1.25	355
		103	3.72	2.33	365
		103	3.72	2.33	365
		108	3.90	2.56	365
	Nitromethane	616	22.2	1.09	321
		611	22.1	1.08	321
		609	22	0.80	321
		295	10.7	1.35	333
		295	10.7	1.35	333
		300	10.8	1.40	333
		159	5.74	2.68	343
		156	5.65	2.60	343
		159	5.74	2.68	343
		97.2	3.51	8.86	353
		94.7	3.42	8.43	353
		87.2	3.15	7.18	353
	Octane	826	29.8	0.05	367
		838	30.3	0.05	367
		844	30.5	0.05	367
		404	14.6	0.06	378
		404	14.6	0.06	378
		399	14.4	0.05	378
		197	7.12	0.07	388
		197	7.12	0.06	388
		197	7.12	0.06	388
		100	3.62	0.08	398
		100	3.62	0.10	398
		103	3.71	0.10	398

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
109	Propylene oxide	381	13.8	0.93	315
		359	13	0.71	315
		359	13	0.82	315
		205	7.40	0.90	324
		210	7.57	0.72	324
		212	7.65	0.73	324
		115	4.15	3.33	334
		115	4.15	1.48	334
		115	4.15	1.48	334
	Pyridine	497	17.9	0.95	365
		492	17.8	0.93	365
		489	17.7	0.81	365
		293	10.6	1.12	375
		280	10.1	1.34	375
		283	10.2	1.37	375
		146	5.28	1.93	387
		143	5.18	1.86	387
		143	5.18	1.86	387
		91.8	3.31	6.79	397
		89.1	3.22	6.40	397
		99.8	3.61	8.00	397
	Vinyl chloride	209	7.54	0.81	297
		217	7.85	0.88	297
		211	7.62	0.83	297
		74.9	2.70	1.60	313
		77.1	2.79	1.70	313
		79.4	2.87	1.79	313
	Acetonitrile	323	4.34	0.52	394
		339	4.56	0.58	394
		358	4.81	0.53	394
		231	3.10	0.59	403
		227	3.05	0.57	403
		220	2.96	0.63	403
		145	1.94	0.60	414
		146	1.97	0.61	414
		146	1.97	0.61	414
		98.3	1.32	0.48	424
		98.3	1.32	0.69	424
		98.3	1.32	0.69	424
	Acrolein	270	3.63	0.48	394
		270	3.63	0.48	394
		269	3.61	0.47	394
		169	2.27	0.53	405
		171	2.29	0.54	405

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
109	Acrolein (cont'd)	172	2.32	0.55	405
		113	1.52	0.48	414
		115	1.54	0.49	414
		113	1.52	0.48	414
		79.0	1.06	0.70	424
		79.0	1.06	0.70	424
		77.2	1.04	0.67	424
	Benzene	326	4.38	0.38	413
		329	4.42	0.42	413
		326	4.38	0.38	413
		206	2.77	0.43	424
		206	2.77	0.43	424
		206	2.77	0.43	424
		134	1.81	0.44	435
		134	1.81	0.55	435
		134	1.81	0.44	435
		91.4	1.23	0.65	446
		91.4	1.23	0.65	446
		93.1	1.25	0.47	446
	Dichloroethane	427	5.74	0.54	409
		429	5.76	0.46	409
		422	5.67	0.45	409
		264	3.55	0.49	420
		266	3.58	0.49	420
		259	3.48	0.53	420
		185	2.49	0.60	429
		185	2.49	0.60	429
		181	2.44	0.58	429
		117	1.57	0.65	440
		117	1.57	0.65	440
		117	1.57	0.94	440
	Ethanol	502	6.75	0.36	374
		484	6.50	0.32	374
		499	6.70	0.34	374
		296	3.98	0.38	383
		308	4.14	0.38	383
		318	4.27	0.37	383
		179	2.40	0.42	393
		180	2.43	0.37	393
		182	2.45	0.38	393
		110	1.47	0.28	404
		111	1.50	0.29	404
		111	1.50	0.29	404

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N ($X10^{-3}$)	Temperature (K)
109	Methyl ethyl ketone	363	4.87	0.41	414
		363	4.87	0.45	414
		360	4.84	0.44	414
		225	3.03	0.46	424
		223	3.00	0.45	424
		222	2.98	0.44	424
		143	1.92	0.44	435
		150	2.02	0.48	435
		156	2.10	0.52	435
		101	1.36	0.69	444
		99.1	1.33	0.67	444
		99.1	1.33	0.67	444
	Nitromethane	310	4.17	0.61	409
		312	4.19	0.55	409
		312	4.19	0.55	409
		208	2.80	0.55	418
		208	2.80	0.66	418
		208	2.80	0.66	418
		140	1.88	0.55	428
		140	1.88	0.72	428
		140	1.88	0.72	428
		95.0	1.28	0.97	440
		93.1	1.25	0.94	440
		96.8	1.30	1.01	440
	Octane	353	4.73	0.18	421
		341	4.58	0.17	421
		339	4.56	0.16	421
		325	4.37	0.14	433
		327	4.40	0.14	433
		332	4.46	0.14	433
		305	4.09	0.09	433
		308	4.14	0.09	433
		306	4.12	0.09	433
		233	3.13	0.14	438
		239	3.21	0.14	438
		242	3.25	0.14	438
		195	2.61	0.16	443
		192	2.58	0.16	443
		195	2.61	0.18	443
		132	1.78	0.20	453
		138	1.86	0.22	453
		140	1.88	0.19	453
	Propylene oxide	281	2.78	0.43	385
		283	3.80	0.32	385
		281	2.78	0.43	385
		178	2.40	0.42	394

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
109	Propylene oxide (Cont'd.)	182	2.44	0.38	394
		190	2.56	0.48	394
		118	1.58	0.54	404
		118	1.58	0.73	404
		118	1.58	0.54	404
		118	1.58	0.54	404
		79.2	1.06	0.73	414
		79.2	1.06	0.73	414
		79.2	1.06	0.47	414
	Pyridine	292	3.92	0.49	458
		492	6.61	1.24	458
		312	4.19	0.50	458
		203	2.73	0.47	468
		203	2.73	0.47	468
		210	2.83	0.60	468
		163	2.18	0.52	477
		159	2.13	0.49	477
		155	2.08	0.47	477
		99.7	1.34	0.62	488
		99.7	1.34	0.62	488
		97.8	1.31	0.60	488
	Vinyl chloride	382	5.13	0.44	335
		383	5.15	0.45	335
		380	5.11	0.44	335
		230	3.10	0.47	346
		230	3.10	0.47	346
		232	3.12	0.48	346
		137	1.84	0.52	357
		139	1.86	0.53	357
		139	1.86	0.53	357
		88.5	1.19	0.69	367
		88.5	1.19	0.69	367
		88.5	1.19	0.48	367
119	Acetonitrile	592	15	0.60	373
		586	14.8	0.59	373
		584	14.8	0.59	373
		323	8.16	0.65	383
		339	8.57	0.71	383
		335	8.47	0.69	383
		188	4.76	0.59	394
		190	4.81	0.76	394
		190	4.81	0.76	394
		119	3.02	1.16	405
		117	2.96	0.72	405
		121	3.07	0.77	405

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
119	Acrolein	820	20.7	0.45	363
		880	22.3	0.14	363
		895	22.6	0.07	363
		405	10.3	0.37	374
		417	10.6	0.34	374
		427	10.8	0.30	374
		229	5.78	0.49	384
		227	5.73	0.48	384
		231	5.84	0.50	384
		125	3.16	0.88	394
		129	3.26	0.94	394
		129	3.26	0.65	394
	Benzene	787	19.9	0.18	375
		822	20.8	0.19	375
		813	20.6	0.19	375
		306	7.75	0.29	394
		308	7.80	0.32	394
		311	7.86	0.29	394
		173	4.38	0.32	404
		177	4.49	0.41	404
		173	4.38	0.32	404
		102	2.57	0.53	414
		104	2.63	0.55	414
		106	2.68	0.58	414
	Dichloroethane	653	16.5	0.39	383
		659	16.7	0.42	383
		655	16.6	0.43	383
		382	9.66	0.44	394
		388	9.82	0.46	394
		213	5.38	0.41	403
		217	5.48	0.50	403
		225	5.70	0.46	403
		113	2.86	0.65	416
		113	2.86	0.65	416
		119	3.02	0.50	416
	Ethanol	652	16.5	0.35	357
		658	16.6	0.28	357
		639	16.2	0.26	357
		305	7.72	0.38	368
		303	7.67	0.38	368
		307	7.77	0.35	368
		156	3.94	0.43	380
		154	3.89	0.42	380
		156	3.94	0.43	380

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
119	Ethanol (Cont'd.)	81.5	2.06	1.03	391
		89.6	2.27	0.31	391
		89.6	2.27	0.70	391
	Methyl ethyl ketone	584	14.8	0.38	392
		590	14.9	0.38	392
		588	14.9	0.69	392
		341	8.64	0.38	400
		339	8.58	0.38	400
		337	8.53	0.41	400
		169	4.27	0.36	412
		175	4.43	0.48	412
		167	4.22	0.72	412
		106	2.69	0.58	421
		106	2.69	0.58	421
		106	2.69	0.58	421
	Nitromethane	581	14.7	0.69	384
		590	14.9	0.66	384
		586	14.8	0.65	384
		349	8.83	0.73	393
		353	8.93	0.75	393
		357	9.03	0.67	393
		212	5.36	0.88	404
		214	5.41	0.71	404
		216	5.46	0.73	404
		119	3.01	1.12	415
		121	3.06	1.16	415
		123	3.12	1.21	415
	Octane	480	12.1	0.02	399
		474	12	0.02	399
		490	12.4	0.02	399
		241	6.11	0.02	409
		241	6.11	0.02	409
		241	6.11	0.02	409
		115	2.91	0.02	420
		115	2.91	0.02	420
		117	2.97	0.02	420
		64.9	1.64	0.02	430
		62.7	1.59	0.02	430
		64.9	1.64	0.02	430
	Propylene oxide	576	14.6	0.34	357
		591	15	0.24	357
		593	15	0.25	357
		309	7.83	0.35	367
		307	7.78	0.35	367
		311	7.88	0.33	367
		124	3.13	0.29	367

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N ($X10^{-3}$)	Temperature (K)
119	**Propylene oxide (Cont'd.)**	137	3.47	0.17	377
		137	3.47	0.17	377
		65.2	1.65	0.12	391
		69.2	1.75	0.27	391
		67.2	1.70	0.26	391
	Pyridine	768	19.4	0.02	502
		729	18.4	0.03	502
		407	10.3	0.02	512
		390	9.87	0.02	512
		407	10.3	0.02	512
		146	3.69	0.01	522
		216	5.47	0.02	522
		192	4.85	0.01	522
		164	4.14	0.01	532
		176	4.46	0.01	532
		179	4.52	0.01	532
	Vinyl chloride	255	6.45	0.81	325
		271	6.85	0.67	325
		296	7.48	0.61	325
		219	5.53	0.59	328
		220	5.58	0.60	328
		225	5.67	0.62	328
		147	3.72	0.76	335
		145	3.68	0.74	335
		147	3.72	0.76	335
		72.4	1.83	0.98	345
		72.4	1.83	0.98	345
		72.4	1.83	0.98	345
140	**Acetonitrile**	766	10.4	0.14	374
		773	10.5	0.14	374
		778	10.6	0.14	374
		435	5.92	0.16	384
		430	5.85	0.15	384
		430	5.85	0.15	384
		225	3.07	0.18	397
		228	3.10	0.18	397
		233	3.17	0.19	397
		139	1.89	0.21	408
		139	1.89	0.21	408
		139	1.89	0.21	408
	Acrolein	1293	17.6	0.08	363
		1307	17.8	0.09	363
		1336	18.2	0.10	363
		611	8.31	0.10	374
		611	8.31	0.09	374

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
140	Acrolein (cont'd.)	621	8.44	0.09	374
		379	5.16	0.10	383
		377	5.13	0.10	383
		372	5.06	0.10	383
		206	2.80	0.11	393
		216	2.94	0.12	393
		211	2.87	0.12	393
		211	2.87	0.12	393
	Benzene	743	10.1	0.02	393
		751	10.2	0.03	393
		425	5.78	0.03	404
		422	5.74	0.03	404
		425	5.78	0.03	404
		155	2.11	0.04	424
		155	2.11	0.04	424
		155	2.11	0.04	424
	Dichloroethane	493	6.71	0.04	390
		506	6.88	0.05	390
		493	6.71	0.05	390
		328	4.47	0.04	400
		333	4.53	0.04	400
		328	4.47	0.04	400
		186	2.53	0.04	411
		186	2.53	0.04	411
		183	2.49	0.04	411
		141	1.92	0.12	421
		141	1.92	0.07	421
		141	1.92	0.10	421
	Ethanol	816	11.1	0.06	367
		852	11.6	0.08	367
		860	11.7	0.05	367
		260	3.54	0.05	379
		258	3.51	0.06	379
		260	3.54	0.06	379
		156	2.12	0.06	389
		158	2.15	0.05	389
		156	2.12	0.06	389
		88.0	1.20	0.09	400
		88.0	1.20	0.09	400
		85.4	1.16	0.08	400
	Methyl ethyl ketone	817	11.1	0.04	392
		832	11.3	0.03	392
		832	11.3	0.03	392
		415	5.65	0.03	402

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N ($X10^{-3}$)	Temperature (K)
140	Methyl ethyl ketone (cont'd.)	410	5.58	0.03	402
		415	5.65	0.04	402
		226	3.07	0.04	414
		223	3.04	0.04	414
		221	3.00	0.04	414
		142	1.93	0.05	423
		139	1.90	0.04	423
		142	1.93	0.05	423
	Nitromethane	873	11.9	0.18	382
		873	11.9	0.16	382
		878	11.9	0.15	382
		465	6.33	0.19	392
		468	6.36	0.17	392
		468	6.36	0.16	392
		294	4.00	0.16	403
		292	3.97	0.16	403
		292	3.97	0.18	403
		292	3.97	0.16	403
		292	3.97	0.16	403
		176	2.40	0.21	415
		176	2.40	0.18	415
		176	2.40	0.18	415
	Octane	276	3.75	0.00	362
		259	3.52	0.01	362
		271	3.68	0.00	362
		55.2	0.75	0.00	393
		55.2	0.75	0.00	393
		55.2	0.75	0.00	393
		97.8	1.33	0.00	393
		95.3	1.30	0.00	393
		97.8	1.33	0.00	393
	Propylene oxide	529	7.20	0.03	367
		527	7.17	0.03	367
		539	7.33	0.03	367
		273	3.72	0.03	379
		273	3.72	0.03	379
		278	3.78	0.03	379
		281	3.82	0.04	379
		163	2.21	0.04	379
		165	2.25	0.04	388
		94.1	1.28	0.05	400
		99.2	1.35	0.05	400
		99.2	1.35	0.05	400

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N ($X10^{-3}$)	Temperature (K)
140	Pyridine	818	11.1	0.06	429
		837	11.4	0.06	429
		831	11.3	0.06	429
		497	6.76	0.06	440
		580	7.89	0.05	440
		558	7.60	0.04	440
		222	3.02	0.08	453
		222	3.02	0.08	453
		222	3.02	0.08	453
		144	1.96	0.12	462
		141	1.92	0.11	462
		141	1.92	0.10	462
	Vinyl chloride	609	8.29	0.04	323
		612	8.32	0.05	323
		545	7.42	0.04	323
		328	4.47	0.05	333
		335	4.56	0.04	333
		333	4.53	0.04	333
		178	2.42	0.05	344
		178	2.42	0.05	344
		178	2.42	0.04	344
		97.1	1.32	0.06	355
		99.4	1.35	0.05	355
		102	1.38	0.06	355
149	Acetonitrile	470	.	0.65	372
		474	.	0.66	372
		476	.	0.60	372
		261	.	0.64	383
		265	.	0.80	383
		265	.	0.80	383
		144	.	1.42	396
		151	.	0.99	396
		151	.	0.99	396
		99.3	.	2.68	403
		97.0	.	2.56	403
		99.3	.	2.68	403
	Acrolein	415	.	0.36	370
		415	.	0.36	370
		400	.	0.33	370
		225	.	0.41	380
		225	.	0.41	380
		225	.	0.41	380
		137	.	0.59	390
		139	.	0.61	390
		137	.	0.59	390

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
149	Acrolein (cont'd.)	82.3	.	0.84	401
		84.6	.	2.00	401
		86.9	.	0.94	401
	Benzene	627	.	0.03	383
		632	.	0.03	383
		627	.	0.03	383
		356	.	0.04	393
		356	.	0.03	393
		361	.	0.04	393
		204	.	0.04	405
		206	.	0.04	405
		202	.	0.04	405
		118	.	0.05	414
		120	.	0.05	414
		122	.	0.05	414
	Dichloroethane	685	.	0.10	384
		685	.	0.09	384
		692	.	0.09	384
		396	.	0.10	394
		399	.	0.10	394
		396	.	0.10	394
		240	.	0.11	403
		240	.	0.10	403
		237	.	0.11	403
		149	.	0.16	413
		149	.	0.16	413
		147	.	0.15	413
	Ethanol	530	.	0.14	358
		525	.	0.15	358
		521	.	0.14	358
		282	.	0.17	368
		282	.	0.17	368
		280	.	0.16	368
		157	.	0.20	378
		157	.	0.20	378
		160	.	0.21	378
		96.7	.	0.22	386
		96.7	.	0.22	386
		99.0	.	0.31	386
	Methylethylketone	713	.	0.07	385
		720	.	0.08	385
		716	.	0.07	385
		399	.	0.08	394
		399	.	0.08	394

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N (X10^{-3})	Temperature (K)
149	Methyl ethyl ketone	397	.	0.08	394
	(cont'd.)	217	.	0.09	404
		219	.	0.09	404
		222	.	0.10	404
		123	.	0.09	414
		126	.	0.11	414
		121	.	0.10	414
	Nitromethane	705	.	0.69	377
		694	.	0.67	377
		694	.	0.67	377
		393	.	0.77	388
		393	.	0.77	388
		395	.	0.78	388
		232	.	0.92	398
		234	.	0.94	398
		234	.	0.94	398
		141	.	2.37	409
		143	.	1.37	409
		143	.	1.37	409
	Octane	234	.	0.00	403
		236	.	0.00	403
		231	.	0.00	403
		141	.	0.01	414
		141	.	0.01	414
		141	.	0.01	414
		74.3	.	0.00	425
		74.3	.	0.00	425
		69.5	.	0.00	425
	Propylene oxide	617	.	0.05	355
		626	.	0.05	355
		622	.	0.05	355
		328	.	0.06	365
		328	.	0.05	365
		326	.	0.05	365
		179	.	0.08	376
		181	.	0.07	376
		181	.	0.07	376
		105	.	0.08	386
		105	.	0.08	386
		108	.	0.08	386
	Pyridine	725	.	0.23	428
		753	.	0.23	428
		801	.	0.18	428
		376	.	0.31	437
		383	.	0.29	437

(continued)

Table G1 (Cont'd.)

Sorbent	Compound	V_N (mL)	V_S (mL/M^2)	N ($X10^{-3}$)	Temperature (K)
149	Pyridine (cont'd.)	386	.	0.27	437
		192	.	0.43	447
		209	.	0.41	447
		209	.	0.41	447
		97.5	.	0.98	458
		97.5	.	0.98	458
		97.5	.	0.98	458
	Vinyl chloride	373	.	0.06	322
		369	.	0.06	322
		367	.	0.07	322
		202	.	0.07	332
		202	.	0.07	332
		202	.	0.09	332
		118	.	0.09	341
		118	.	0.09	341
		120	.	0.09	341
		68.7	.	0.13	352
		70.8	.	0.14	352
		68.7	.	0.13	352

APPENDIX H

PLOTS OF Log V_n *vs*. 1/°K (LEVEL II DATA)

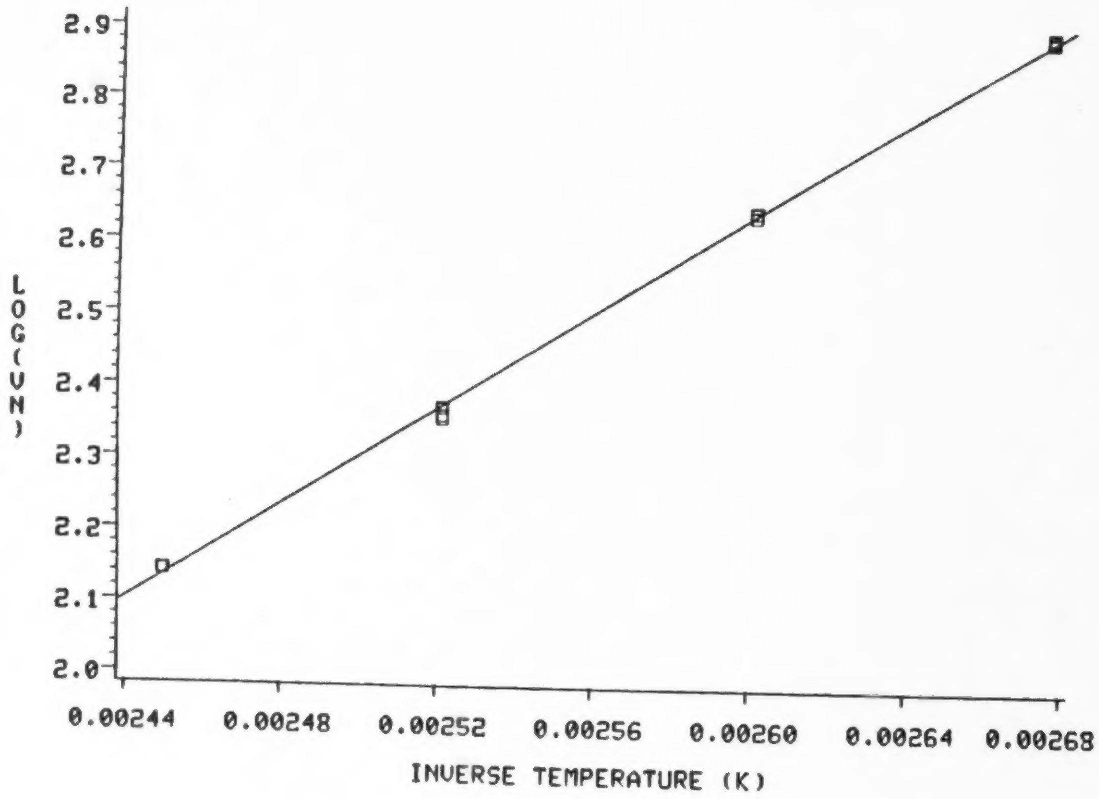


Figure III. Sorbent = 140 Compound = acetonitrile

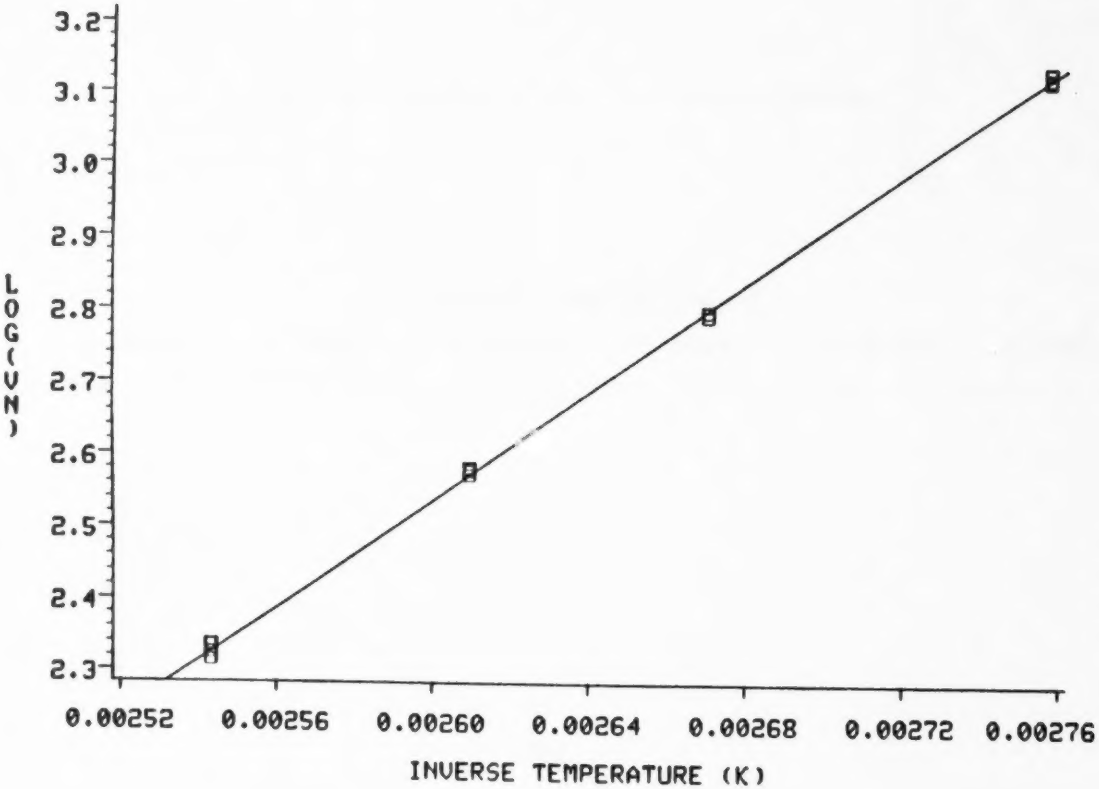


Figure 112. Sorbent = 140 Compound = acrolein

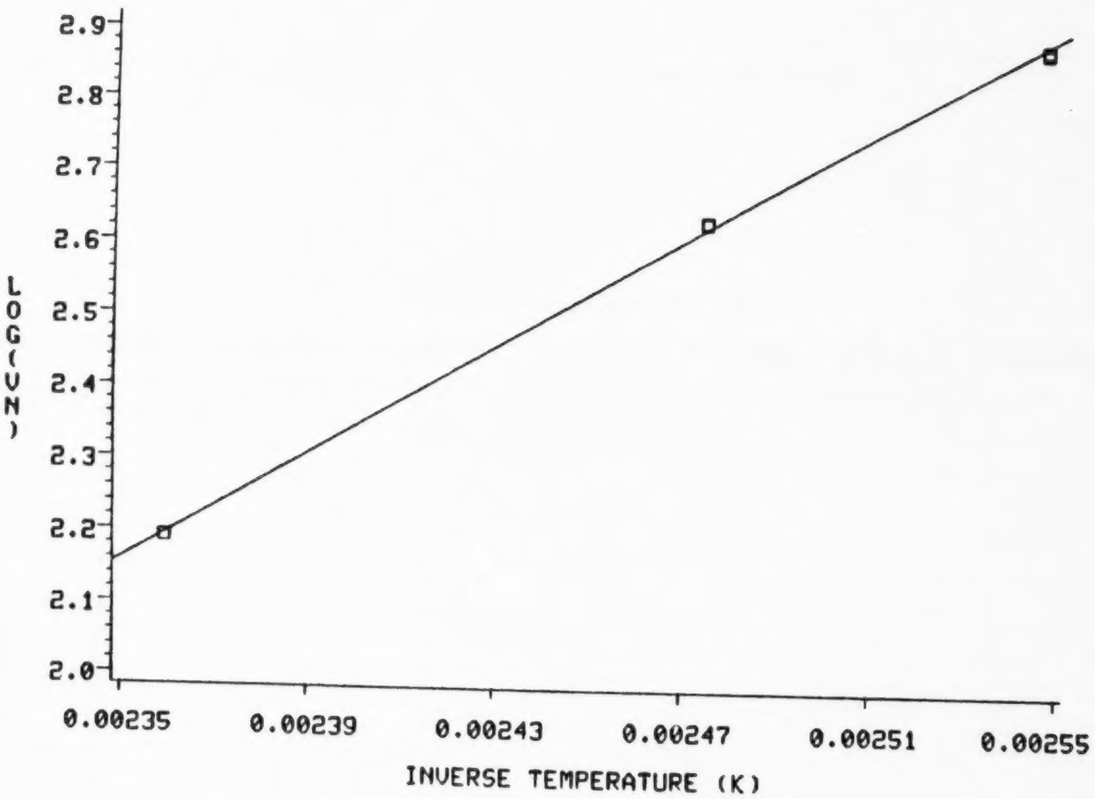


Figure 113. Sorbent = 140 Compound = benzene

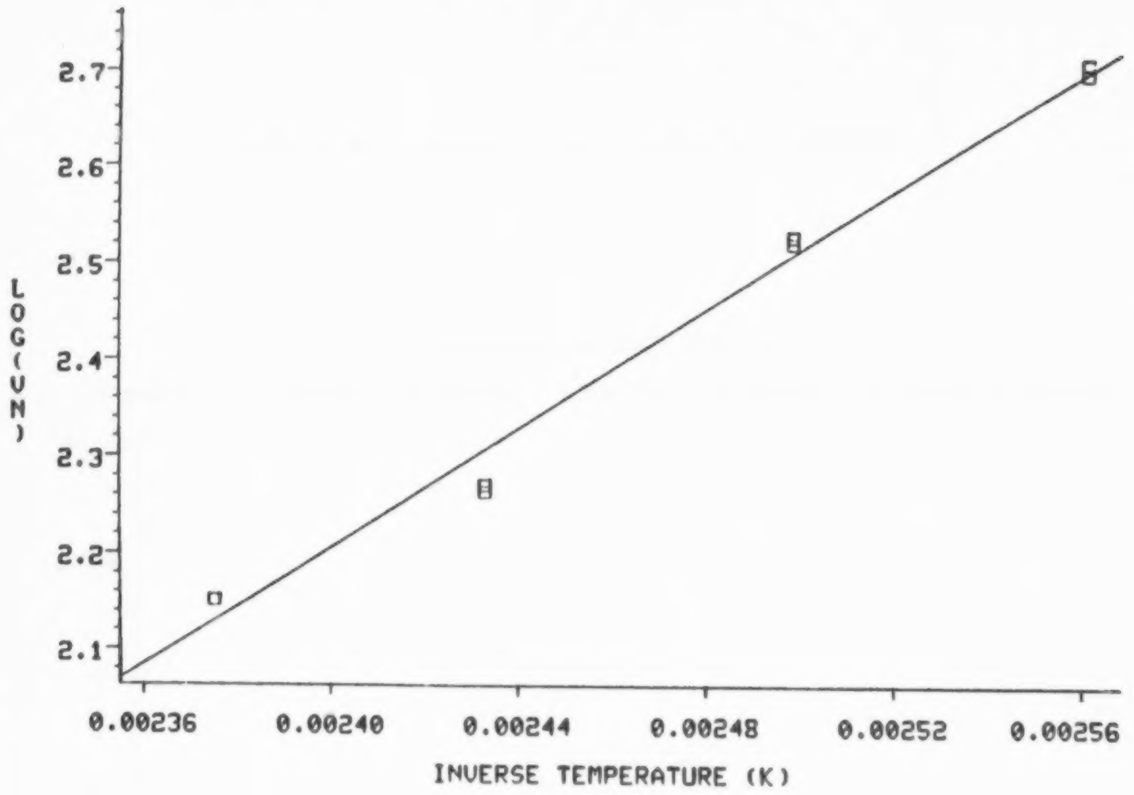


Figure 114. Sorbent = 140 Compound = dichloroethane

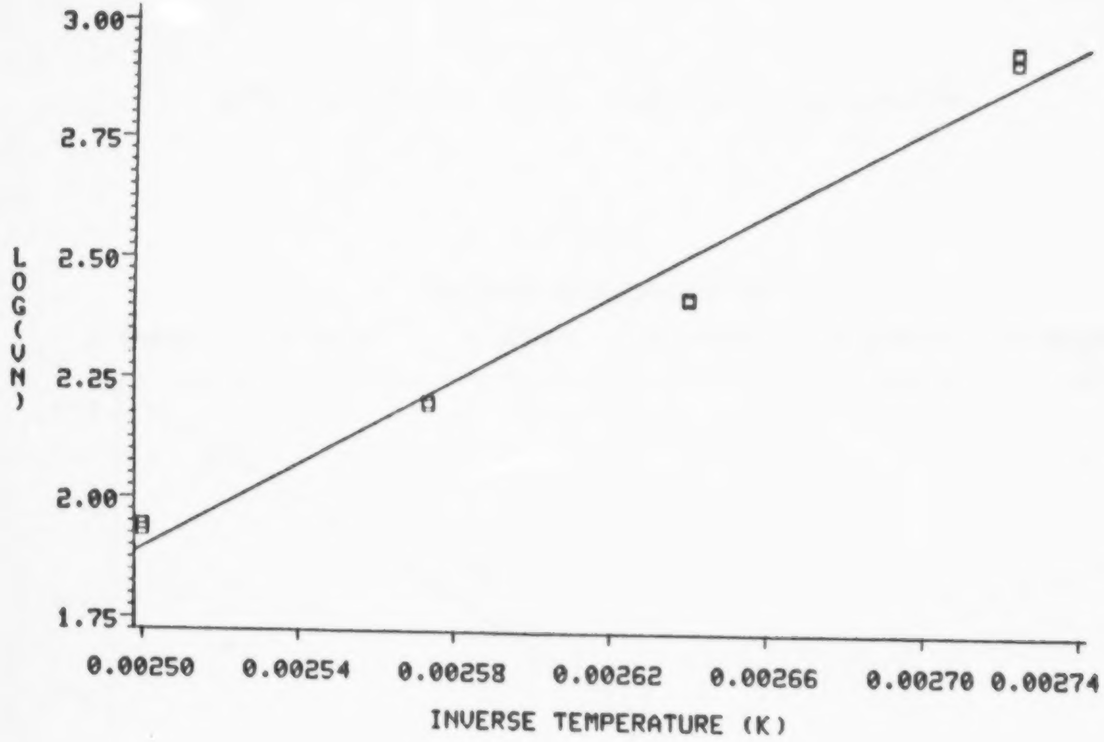


Figure 115. Sorbent = 140 Compound = ethanol

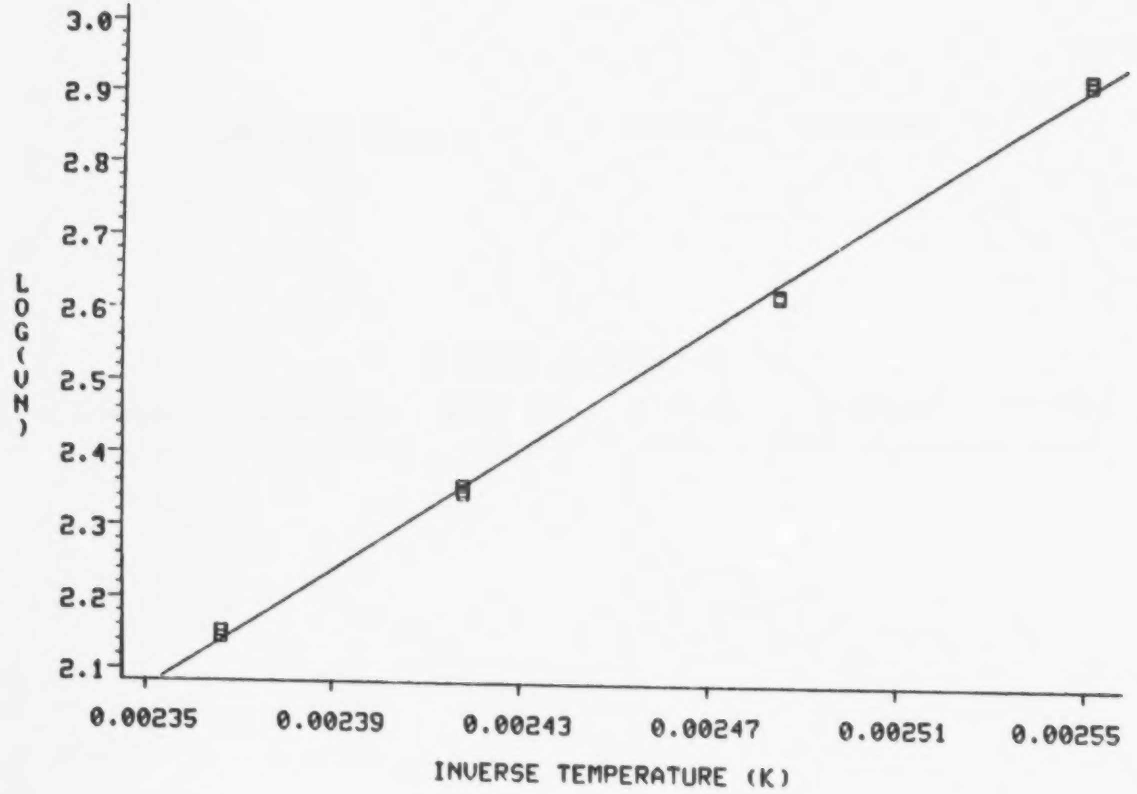


Figure H6. Sorbent = 140 Compound = methyl ethyl ketone

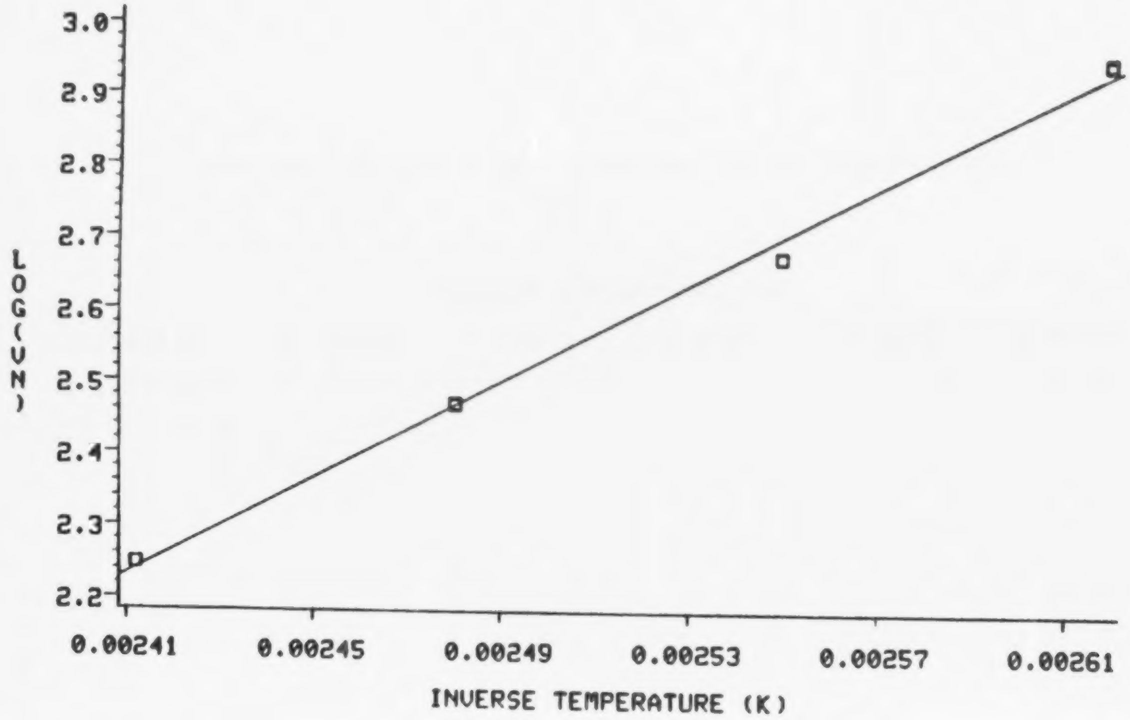


Figure 117. Sorbent = 140 Compound = nitromethane

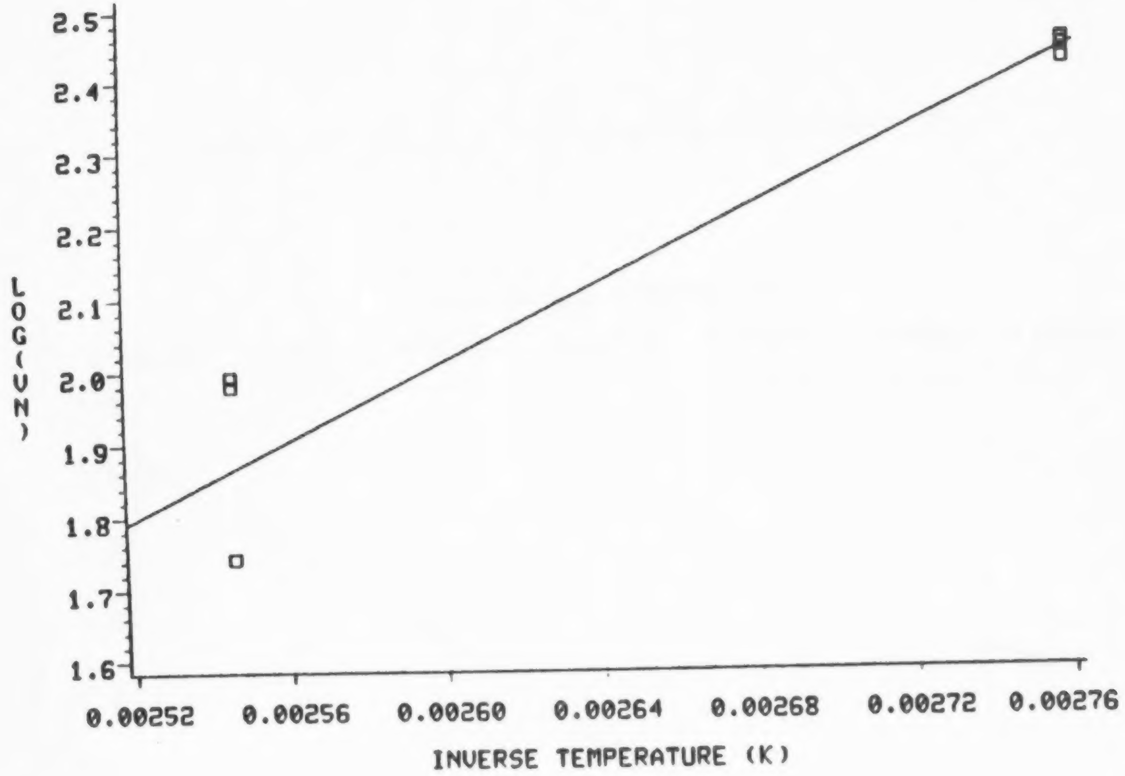


Figure H8. Sorbent = 140 Compound = octane

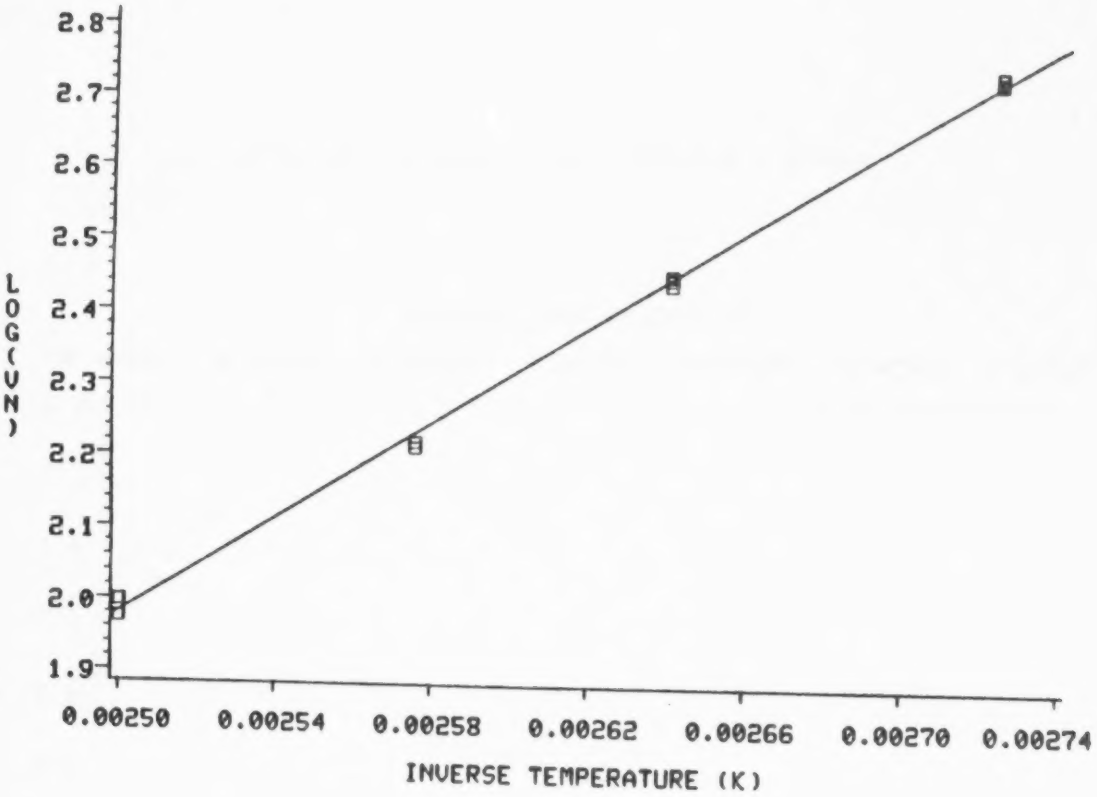


Figure 119. Sorbent = 140 Compound = propylene oxide

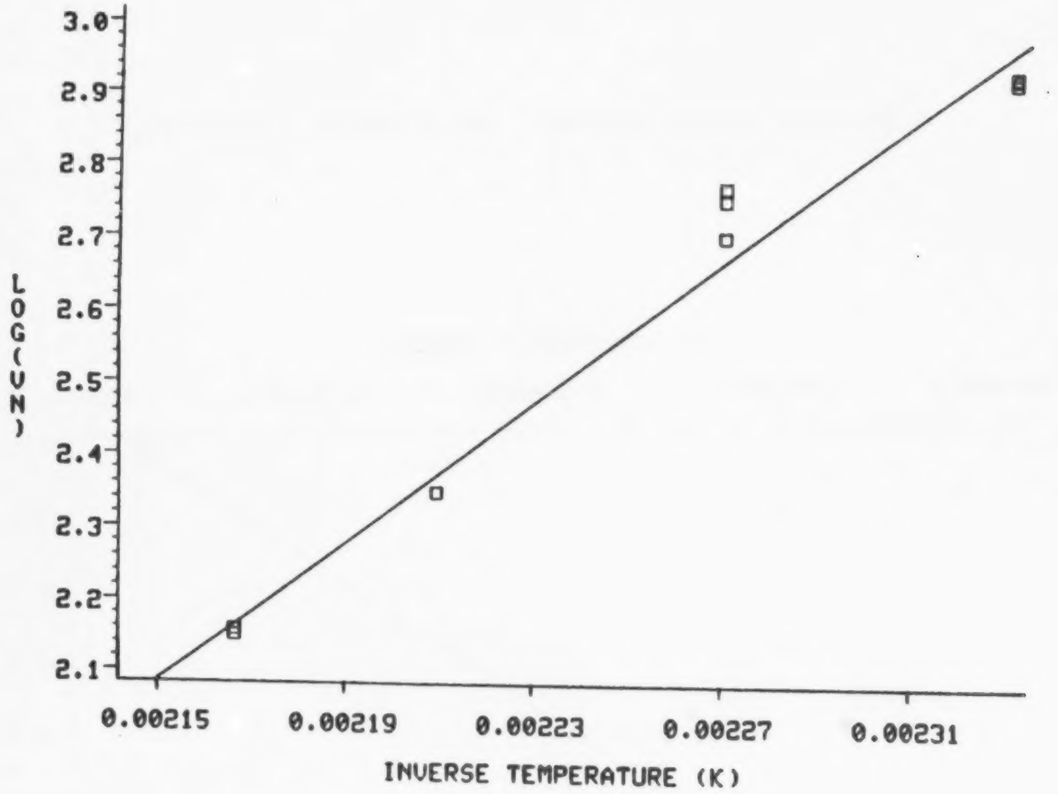


Figure H10. Sorbent = 140 Compound = pyridine

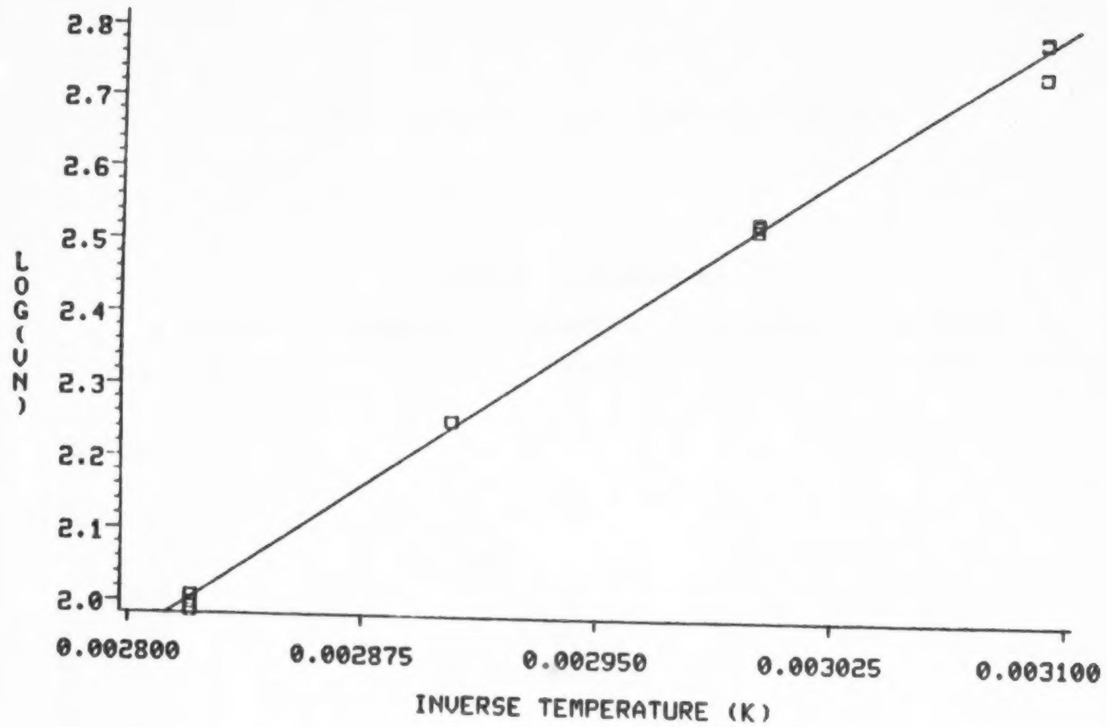


Figure H11. Sorbent = 140 Compound = vinyl chloride

APPENDIX I

RETENTION VOLUMES FOR TEST SUBSTANCES ON MULTI-POLYIMIDE BATCHES

(LEVEL II DATA)

Table II. RETENTION VOLUMES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-115

	Sorbent							
Test substance	Tenax	115	138	140	156	Mean*	s.d.*	%CV*
C7-C10	270-400	490	190	350	180	300	148	49
Benzene	240	380	350	410	320	370	39	11
Ethanol	77	260	270	290	240	260	22	8
Methyl ethyl ketone	210	380	350	400	310	360	36	10
Nitromethane	160	370	390	390	310	360	40	11
Pyridine	300	490	520	520	420	490	50	10
Acetonitrile	120	340	360	350	280	330	36	11
Dichloroethane	200	380	340	380	300	350	38	11
Vinyl chloride	49	180	120	160	130	150	25	17

*For polyimide sorbents.

Table I2. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-115

	Sorbent							
Test substance	Tenax	115	138	140	158	Mean*	s.d.*	%CV*
C7-C10	940-2,580	44	5	15	5	17	18	104
Benzene	560	160	15	250	19	112	116	103
Ethanol	90	150[a]	22	46	34	34	12	35
Methyl ethyl ketone	750	350	19	250	85	175	151	86
Nitromethane	520	270	100	990[a]	190	188	83	44
Pyridine	1,050	390	150	1,050	160	438	425	97
Acetonitrile	450	8,460[a]	92	200	190	161	60	37
Dichloroethane	770	360	39	220	95	178	143	80
Vinyl chloride	88	36	16	68	30	38	22	59

[a] This point was rejected because Q_{exp} was larger than Q_{table}.

Q_{table} at 90% confidence for 4 points = 0.76

$$Q = \frac{\text{suspect value - nearest value}}{\text{largest value - smallest value}}$$

*For polyimides.

Table I3. RETENTION VOLUMES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-124

	Sorbent							
Test substance	Tenax	124	145	161	162	Mean*	s.d.*	%CV*
C7	267	163	125	126	145	140	18	13
C8	318	220	171	176	205	193	23	12
C9	362	273	209	222	258	241	30	12
C10	402	323	246	262	315	287	38	13
Benzene	235	295	225	242	265	257	30	12
Ethanol	77	215	196	206	235	213	17	8
Methyl ethyl ketone	206	300	238	252	293	271	30	11
Nitromethane	162	323	267	278	335	301	33	11
Pyridine	299	460	390	408	510	442	54	12
Acetonitrile	116	278	232	242	290	261	28	11
Dichloroethane	202	293	230	234	275	258	31	12
Vinyl chloride	49	100	86	90	80	89	8	9

*For polyimide sorbents.

Table I4. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-124

	Sorbent							
Test substances	Tenax	124	145	161	162	Mean*	s.d.*	%CV*
C7	939	108	117	87	102	104	13	12
C8	1,248	281	317	215	222	259	49	19
C9	1,967	475	527	493	385	470	61	13
C10	2,575	138	142	181	120	145	26	18
Benzene	557	25	21	28	16	23	5	23
Ethanol	90	33	32	52	20	34	13	39
Methyl ethyl ketone	749	60	43	43	30	44	12	28
Nitromethane	518	230	1,070	495	319	529	38	71
Pyridine	1,047	339	264	220	144	242	82	34
Acetonitrile	452	342	586	723	318	492	20	40
Dichloroethane	771	57	33	34	21	36	15	41
Vinyl chloride	88	10	13	9	4	9	4	42

*For polyimides.

Table I5. RETENTION VOLUMES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-109

	Sorbent							
Test substance	Tenax	109	164	166	170	Mean	s.d.	%CV
C7	267	435	385	289	310	355	68	19
C8	318	493	445	332	355	406	76	19
C9	362	545	494	369	392	450	83	18
C10	402	593	536	402	425	489	91	19
Benzene	235	440	398	294	320	363	59	16
Ethanol	77	325	287	215	234	265	50	19
Methyl ethyl ketone	206	448	398	298	324	367	69	19
Nitromethane	162	428	383	291	314	354	63	18
Pyridine	299	555	511	382	411	465	82	18
Acetonitrile	116	370	385	326	273	339	50	15
Dichloroethane	202	488	400	302	324	379	84	22
Vinyl chloride	49	208	173	127	142	163	36	22

Table I6. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-109

	Sorbent							
Test substance	Tenax	109	164	166	170	Mean*	s.d.*	%CV*
C7	939	1,890	804	1,370	1,010	1,270	412	32
C8	1,248	2,430	1,070	1,430	1,320	1,560	517	33
C9	1,967	3,880	1,770	1,760	2,000	2,350	1,020	43
C10	2,575	6,240	2,320	3,020	2,350	3,482	1,866	54
Benzene	557	1,940	2,880	3,650	2,990	2,860	610	21
Ethanol	90	1,200	1,490	1,340	900	1,230	251	20
Methyl ethyl ketone	749	5,130	4,150	5,850	3,620	4,690	996	21
Nitromethane	518	3,250	7,840	9,870	11,520	8,120	3,578	44
Pyridine	1,047	1,630	2,680	2,400	4,220	2,730	1,086	40
Acetonitrile	452	1,560	3,890	6,970	3,870	4,070	2,220	54
Dichloroethane	771	4,230	4,200	6,010	4,410	4,710	870	18
Vinyl chloride	88	1,100	784	1,380	1,330	1,150	272	24

[a] These points were discarded by the Q test.

If $Q_{suspect} > Q_{table}$, point can be discarded

$$Q = \frac{\text{suspect value - nearest value}}{\text{largest value - smallest value}}$$

$$Q_{table} = 0.76 \text{ for 4 points}$$

*For polyimides.

Table I7. RETENTION VOLUMES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-119

	Sorbent							
Test substance	Tenax	119	154	157	159	Mean	s.d.	%CV
C7	267	305	295	285	356	310	32	10
C8	318	383	310	323	410	357	48	13
C9	362	428	346	357	454	396	53	13
C10	402	468	372	386	494	430	60	14
Benzene	235	335	293	310	375	328	36	11
Ethanol	77	298	235	239	291	266	33	13
Methyl ethyl ketone	206	368	314	321	400	351	41	12
Nitromethane	162	350	314	327	393	346	35	10
Pyridine	299	505	385	450	504	461	57	12
Acetonitrile	116	310	284	291	358	311	33	11
Dichloroethane	202	350	312	319	393	344	37	11
Vinyl chloride	49	128	137	139	156	140	12	8

Table I8. NUMBER OF THEORETICAL PLATES FOR TEST SUBSTANCES ON BATCHES OF POLYIMIDE PI-119

	Sorbent							
Test substance	Tenax	119	154	157	159	Mean*	s.d.*	%CV*
C7	939	492	1,540	900	1,020	988	430	44
C8	1,248	936	1,090	1,430	1,360	1,204	230	19
C9	1,967	1,440	1,870	2,210	2,120	1,910	345	18
C10	2,575	1,730	1,300	1,360	1,600	1,500	202	13
Benzene	557	718	973	4,250	3,700	2,410	1,820	76
Ethanol	90	1,160	3,910	1,760	3,480	2,577	1,325	51
Methyl ethyl ketone	749	3,460	3,120	3,170	4,200	3,488	498	14
Nitromethane	518	3,140	3,120	13,150	6,320	6,432	4,724	73
Pyridine	1,047	33	1,390	359	1,660	860	786	91
Acetonitrile	452	1,710	3,650	5,850	3,360	3,643	1,702	47
Dichloroethane	771	2,180	4,410	7,060	4,040	4,422	2,011	45
Vinyl chloride	88	416	1,740	3,410	1,300	1,716	1,256	73

*For polyimides.

APPENDIX J
POROSIMETRIC MEASUREMENTS
(LEVEL II DATA)

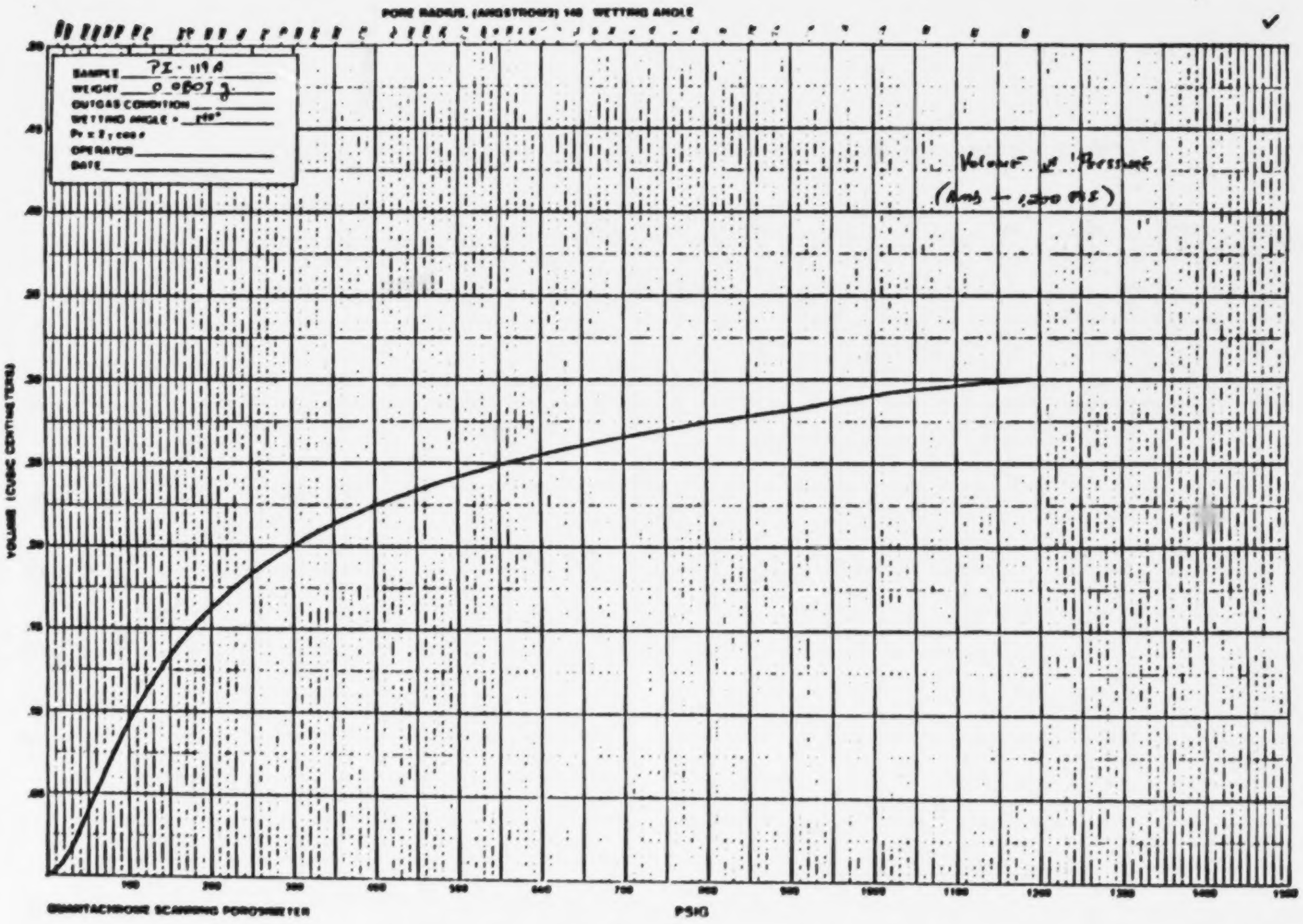


Figure J1. Volume vs. Pressure (Ambient to 1200 psi) for PI-119A.

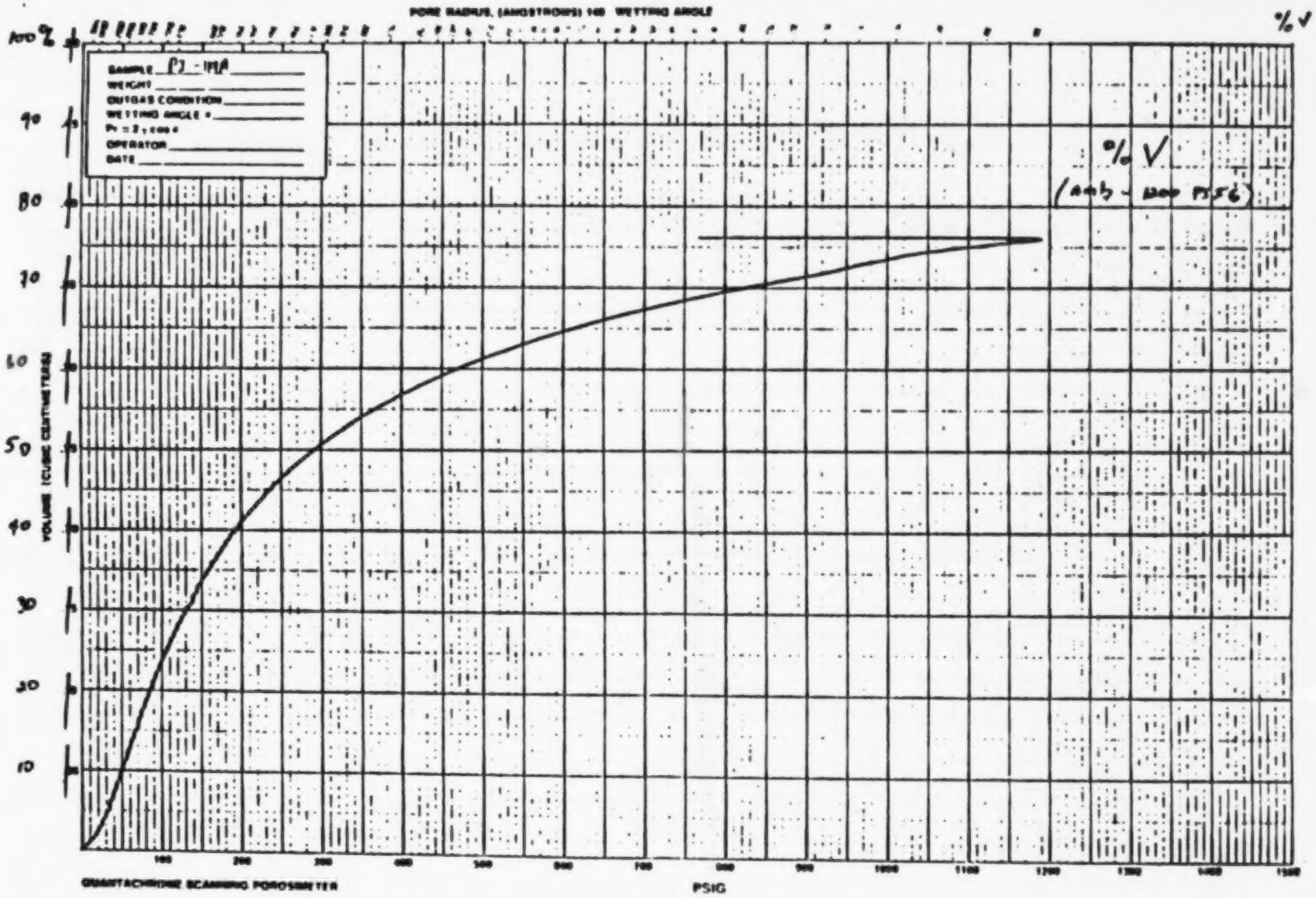


Figure J2. Percent Volume (ambient to 1200 psi) for PI-119A.

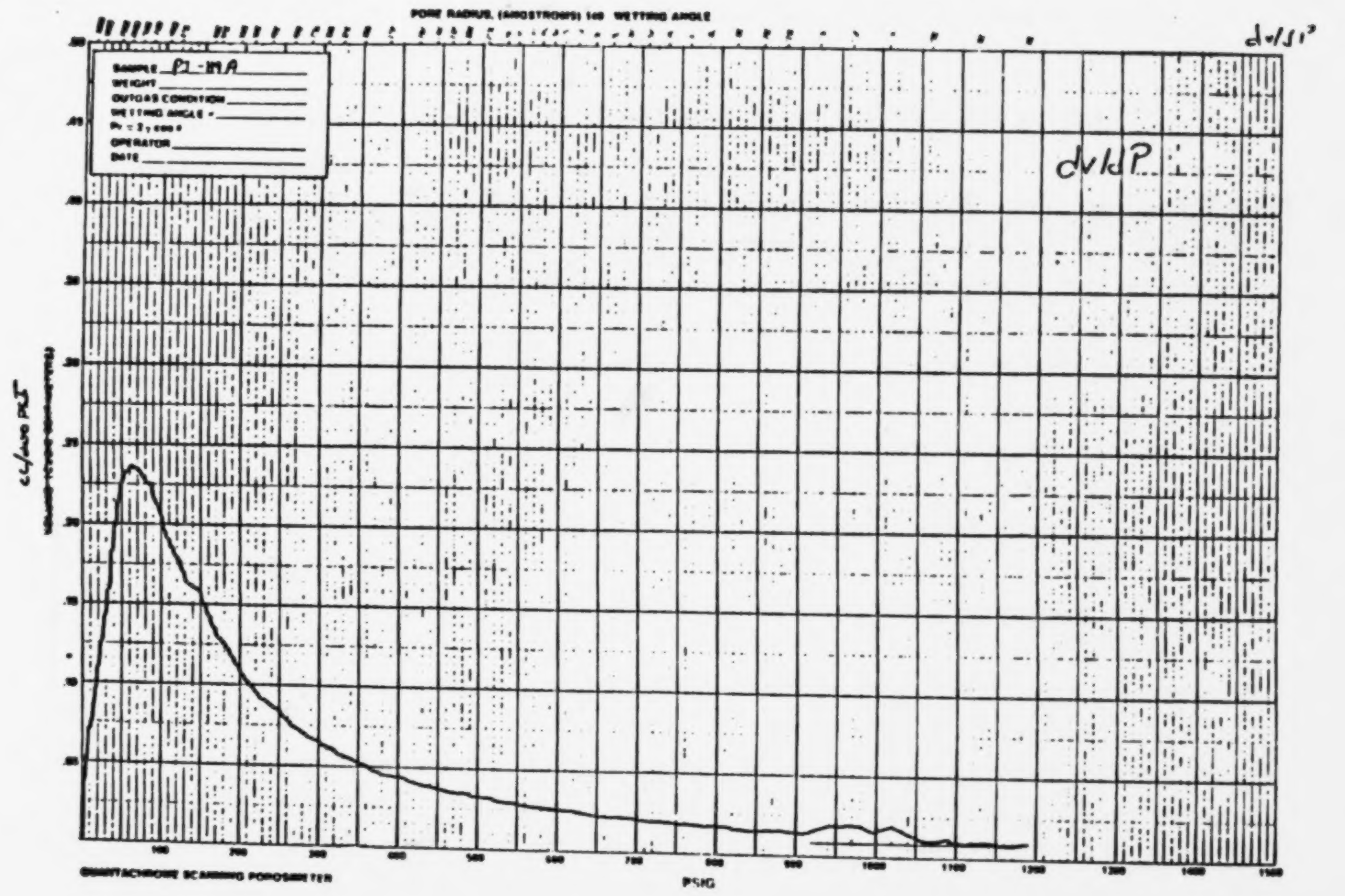


Figure J3. Estimation of dV/dP (ambient to 1200 psi) for PI-119A.

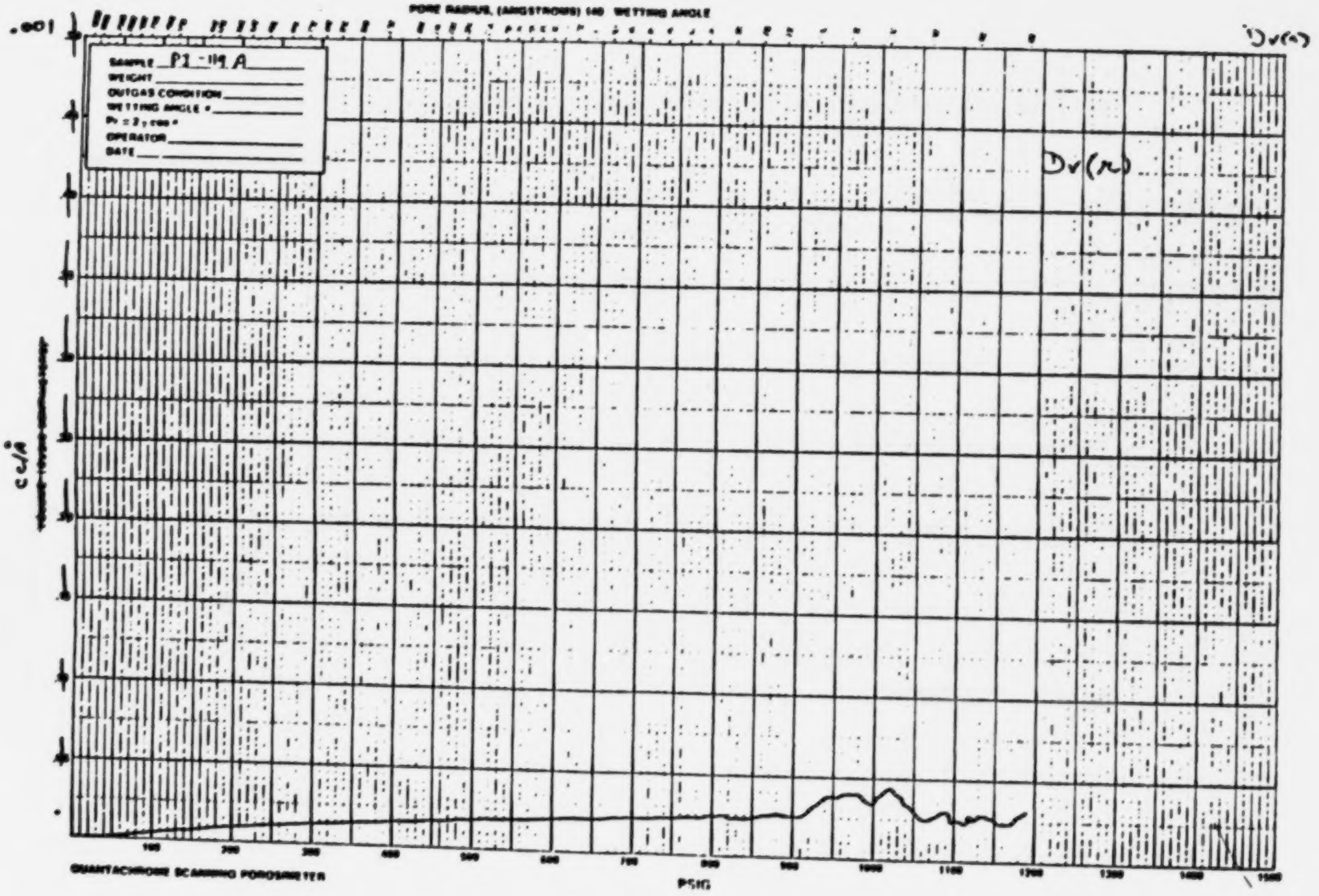
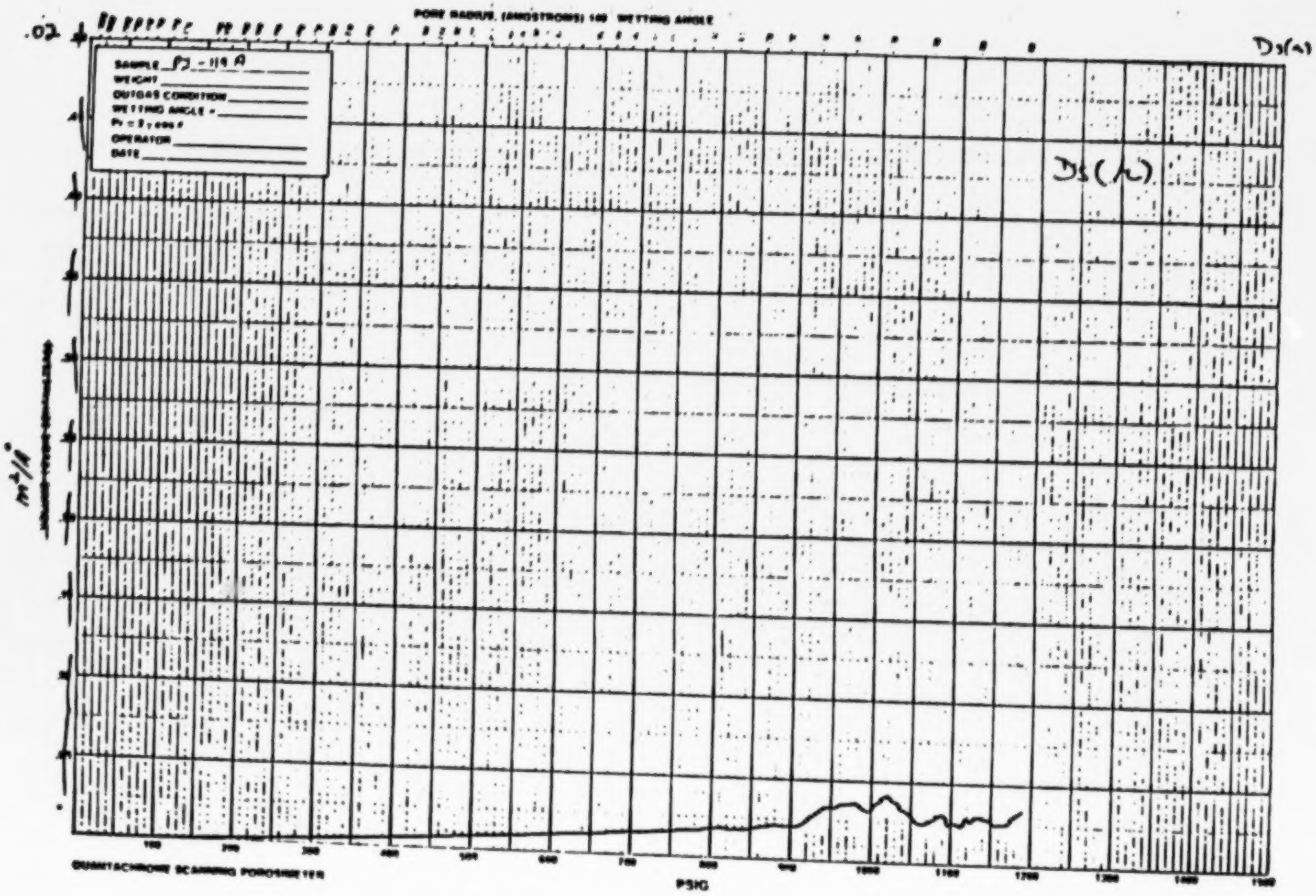
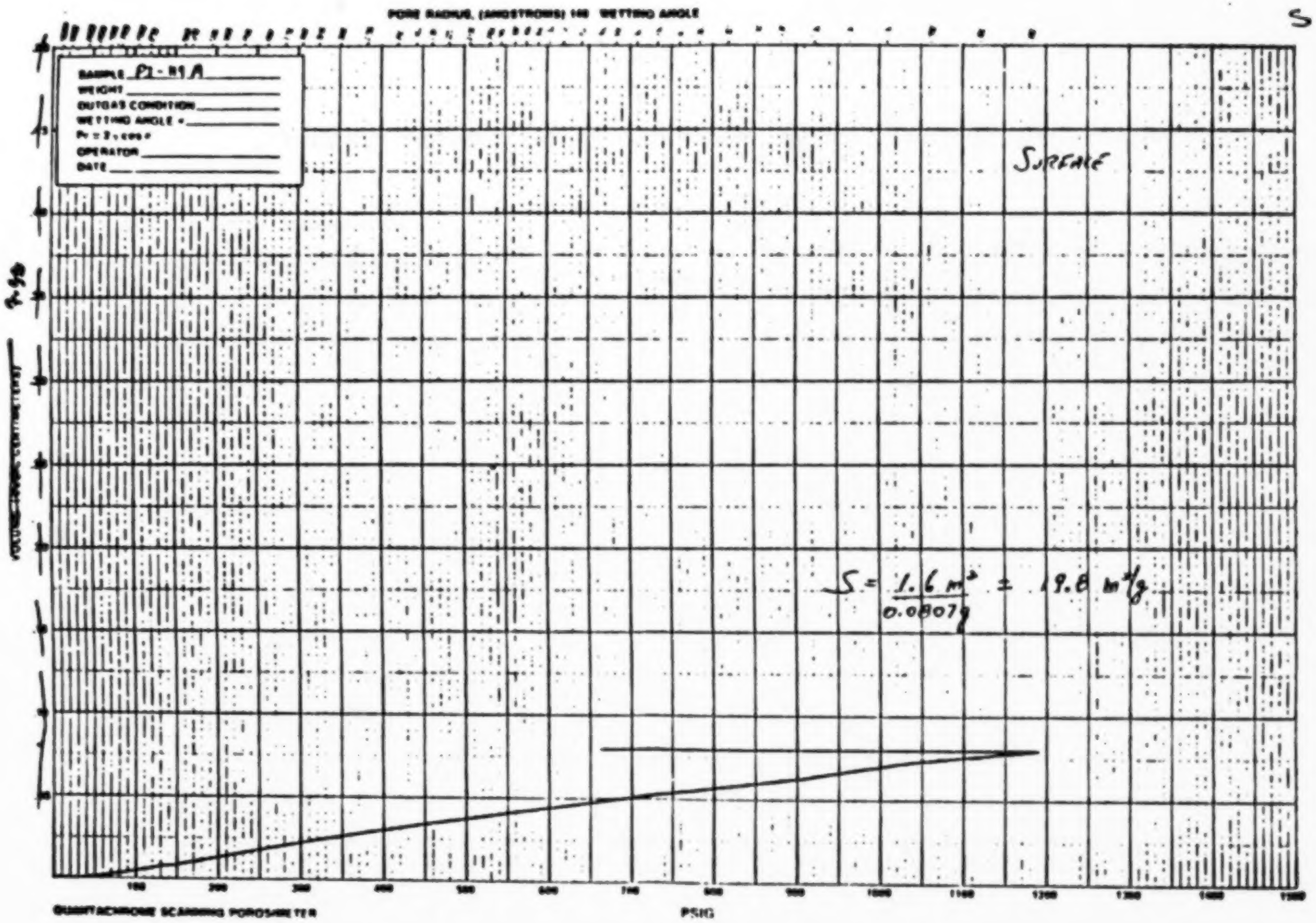


Figure J4. Estimation of Dv(r) (ambient to 1200 psi) for PI-119A.



SAMPLE PI - 119 A
WEIGHT
OUTGAS CONDITION
WETTING ANGLE =
OPERATOR
DATE

Figure J5. Estimation of Ds(r) (ambient to 1200 psi) for PI-119A.



$S = \frac{1.6\ m^2}{0.0807\ g} = 19.8\ m^2/g$

Figure J6. Estimation of surface area (ambient to 1200 psi) for PI-119A.

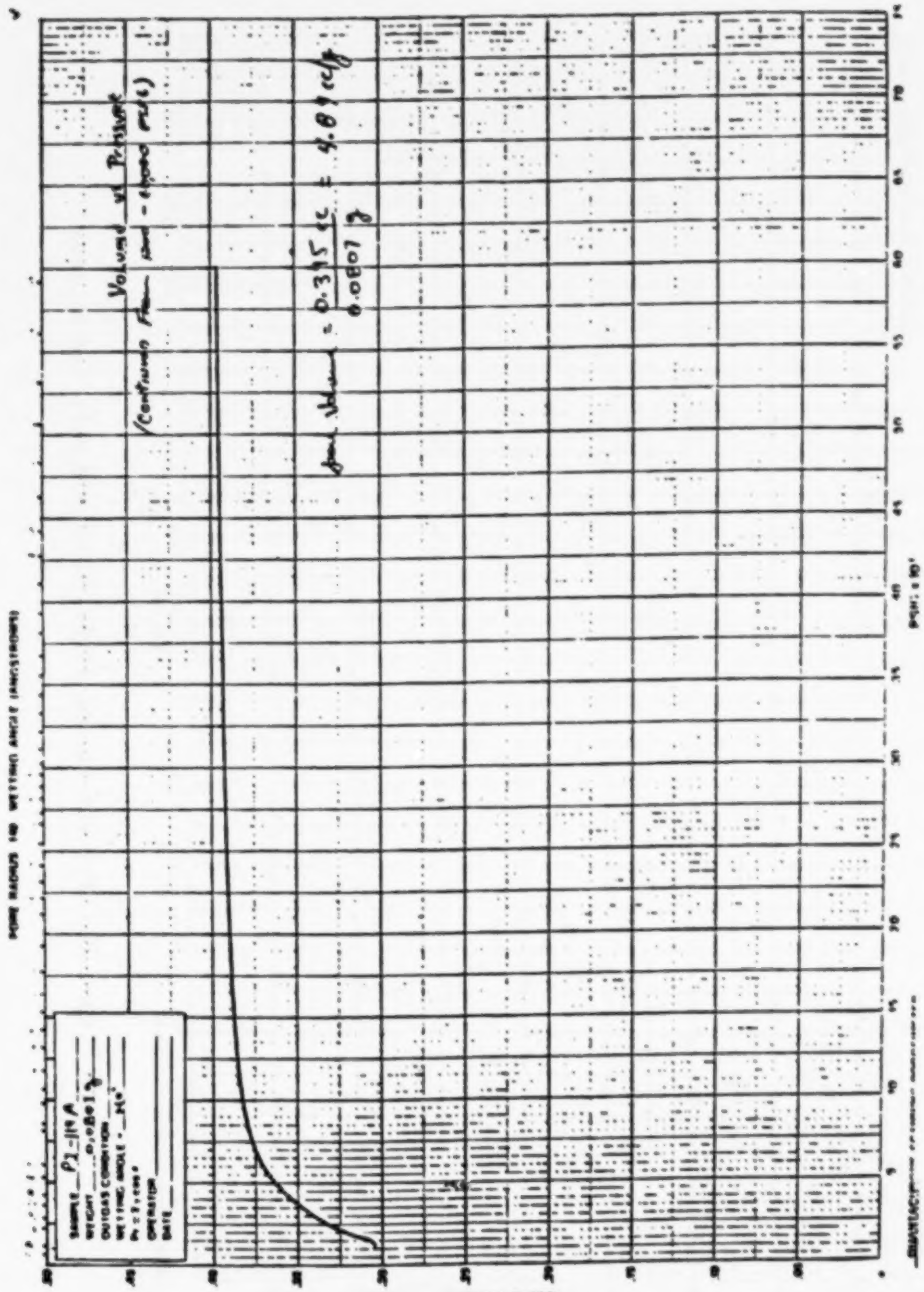


Figure J7. Volume vs. pressure (1200-60,000 psi) for PI-119A.

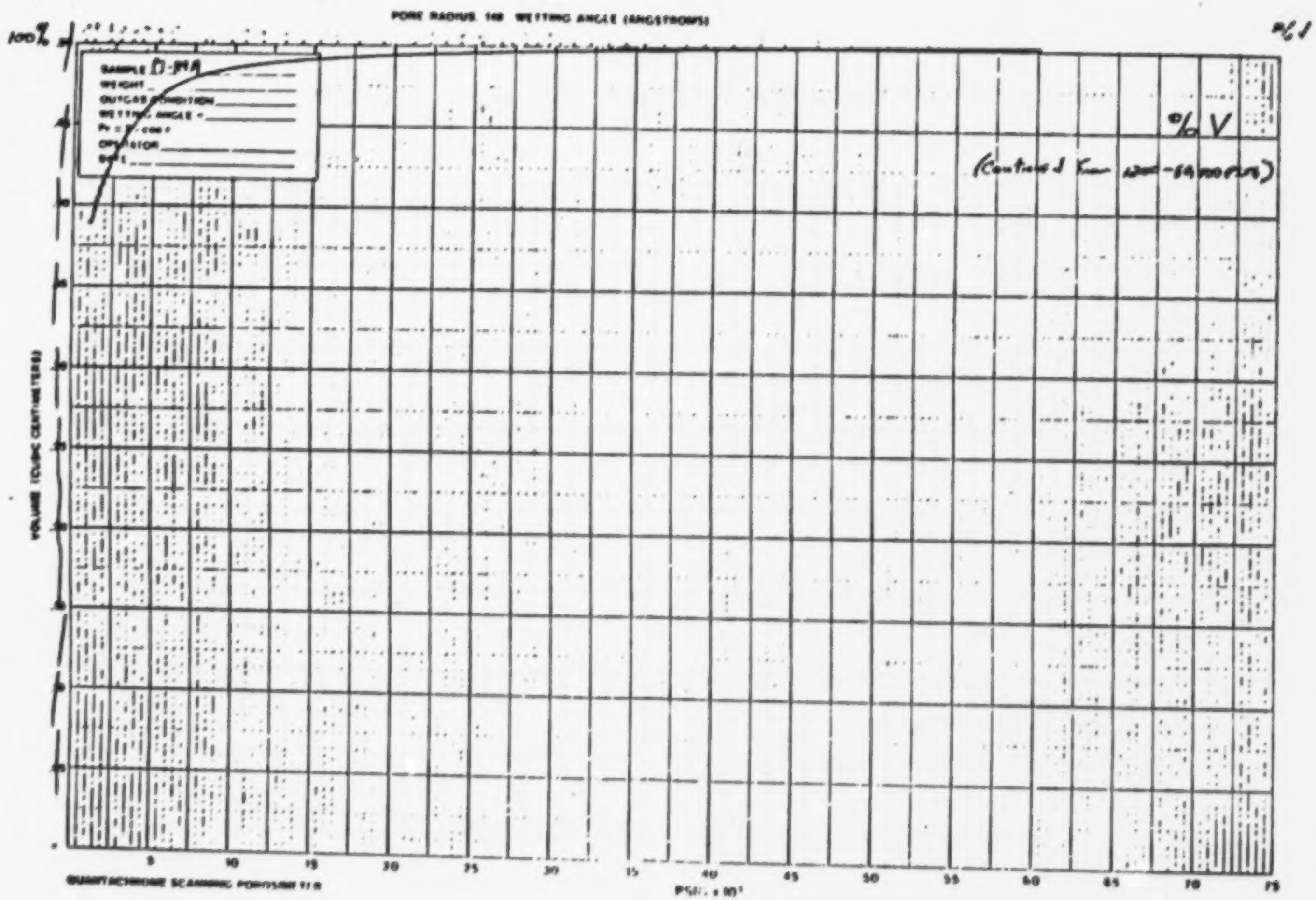


Figure J8. Percent volume (1200 to 60,000 psi) for PI-119A.

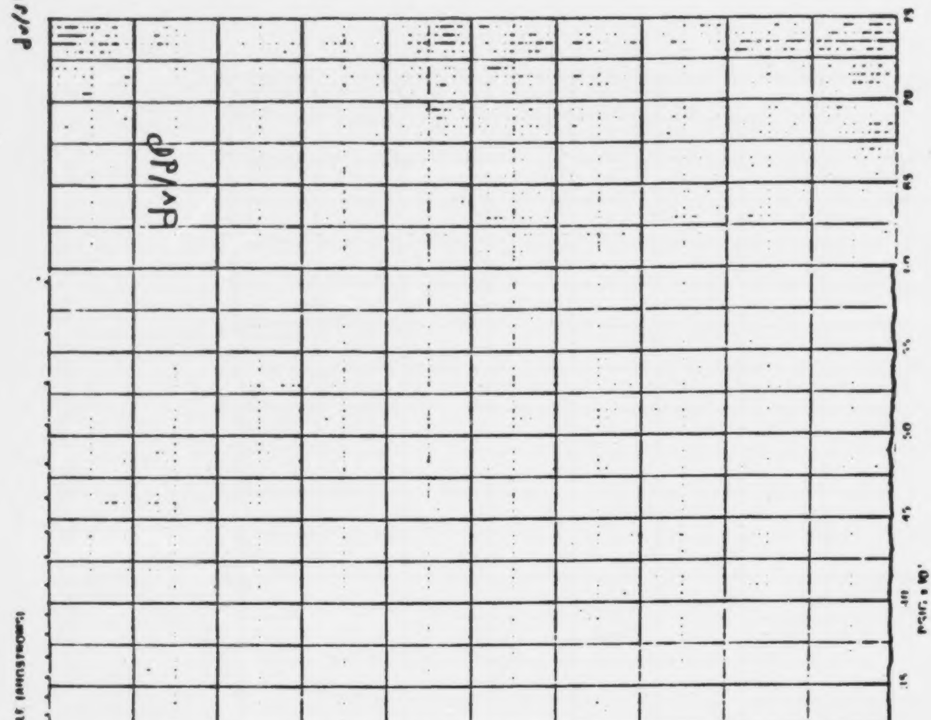


Figure J9. Estimation of dV/dP (1200 to 60,000) for PI-119A.

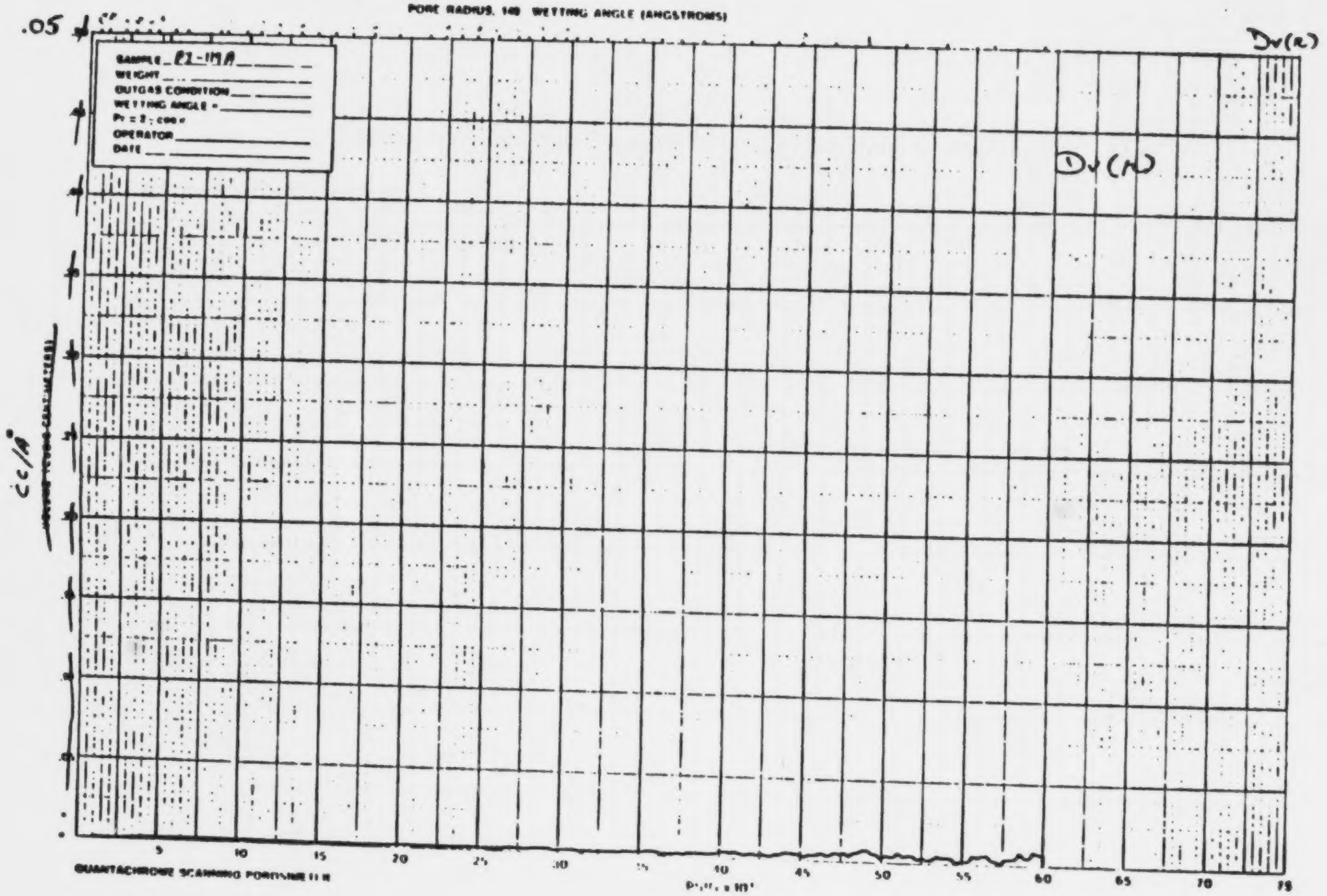


Figure J10. Estimation of Dv(r) (1200 to 60,000 psi) for PI-119A.

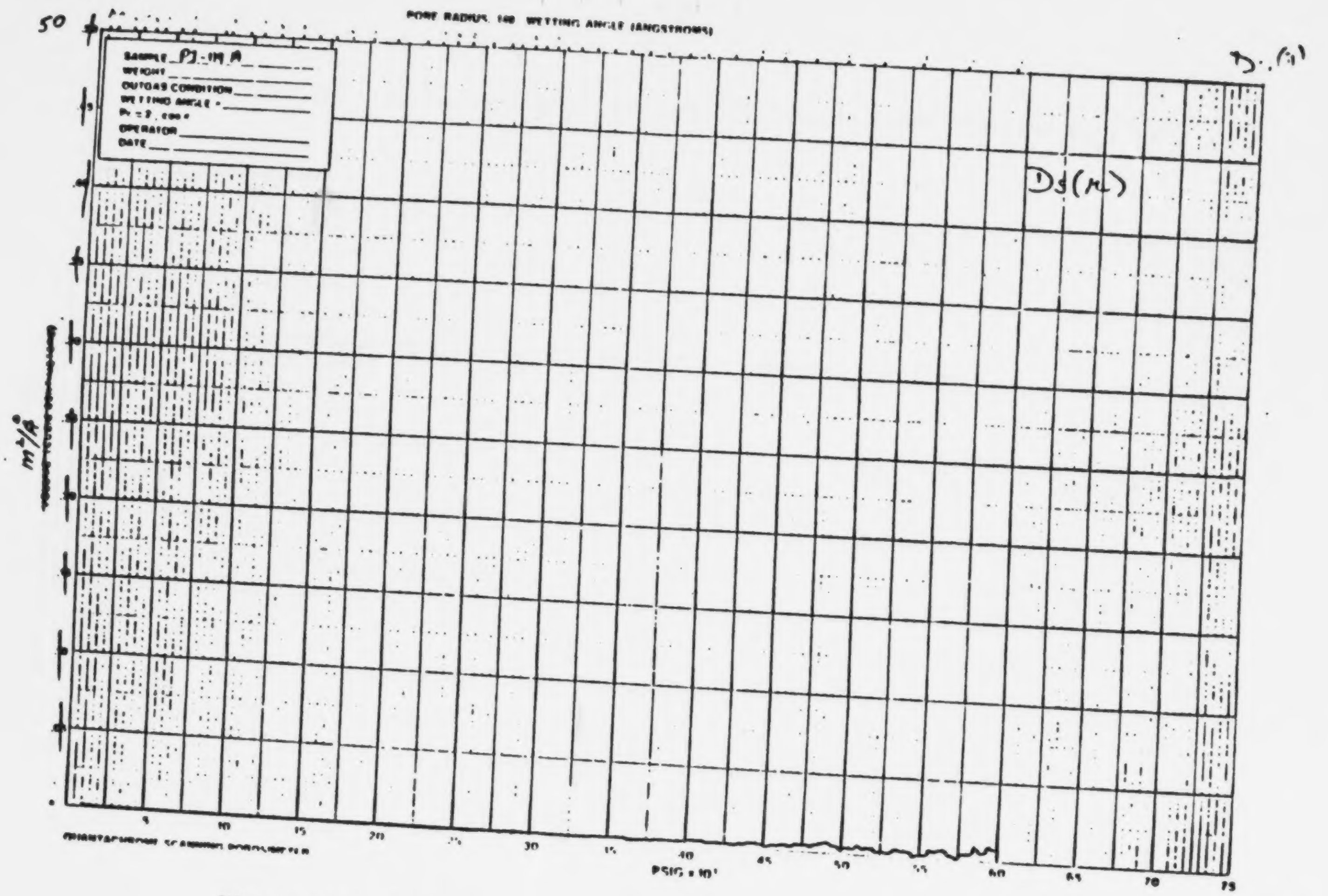


Figure J11. Estimation of Ds(r) (1200 to 60,000 psi) for PI-119A.

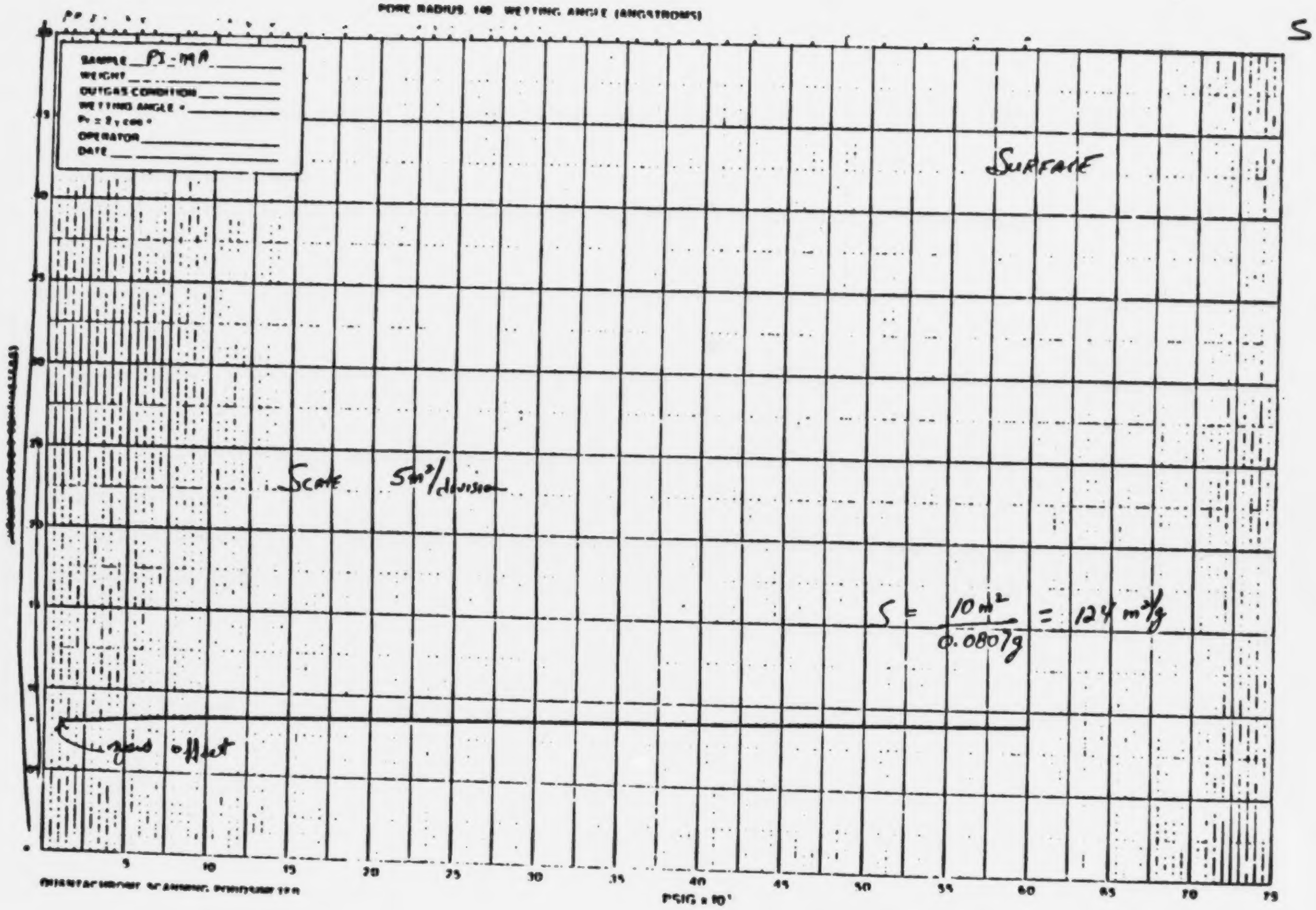


Figure J12. Estimation of surface area (1200 to 60,000 psi) for PI-119A.

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                    MICROMERITICS AUTO-PORE 9200 V2.01            PAGE 1

RESEARCH TRIANGLE INSTITUTE         #43890-061-S             LP 1:6:43 4/9/38
PI - 119                          MAL#1260  -1               HP 2:30:28 4/9/38
PNTR NUMBER   +11

   LP EQUILIBRATION =    +5.0000 SEC         PNTR CONSTANT =   +22.5100 MICRO-L/RF
   HP EQUILIBRATION =   +10.0000 SEC                 THETA =  +130.0000
      SAMPLE WEIGHT =    +0.1025 G                   GAMMA =  +485.0000 DYNES/CM
        PNTR WEIGHT =   +72.0265 G        INITIAL PRESSURE =    +1.4138 PSIA
 PNTR+SAMPLE WEIGHT =   +72.1290 G           PORE DIAMETER =  +125.0220 MICRO-M
PNTR+SAMPLE+MERCURY =  +146.0030 G         MERCURY DENSITY =   +13.5335 G/CC
        PNTR VOLUME =    +6.2876 CC


INTRUSION (PRESSURIZATION) DATA SUMMARY

        TOTAL INTRUSION VOLUME =     +7.3816 CC/G
               TOTAL PORE AREA =   +162.1570 SQ-M/G
MEDIAN PORE DIAMETER  (VOLUME) =     +1.8135 MICROMETERS
MEDIAN PORE DIAMETER  (AREA)   =     +0.0285 MICROMETERS
  AVERAGE PORE DIAMETER (4V/A) =     +0.1823 MICROMETERS
                  BULK DENSITY =     +0.1222 G/CC
   APPARENT (SKELETAL) DENSITY =     +1.2580 G/CC

% CAPILLARY =   +88.5601
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                    MICROMERITICS AUTO-PORE 9200 V2.01              PAGE 2

RESEARCH TRIANGLE INSTITUTE           #43880-061-S          LP 1:6:43 4/9/38
PI - 119                             MAL#1260  -1           HP 2:30:28 4/9/38
PNTR NUMBER   +11

   PRESSURE       PORE      INTRUSION      PORE        MEAN
     PSIA       DIAMETER     VOLUME       SURFACE    DIAMETER          DV
                 MICRO-M      CC/G        SQ-M/G      MICRO-M

        +1.4   +124.3780    +0.0054      +0.0002    +124.7000       +0.0054
        +2.0    +87.4251    +0.2789      +0.0105    +105.8010       +0.2735
        +3.0    +58.4318    +1.3033      +0.0663     +73.4284       +1.0244
        +4.0    +44.6014    +1.8557      +0.1088     +52.0166       +0.5524
        +5.5    +32.3017    +2.2855      +0.1545     +38.4515       +0.4398
        +7.0    +25.3458    +2.5208      +0.1858     +28.8238       +0.2253
        +8.4    +20.9458    +2.6388      +0.2062     +28.1457       +0.1180
       +10.5    +16.8855    +2.7515      +0.2300     +18.9155       +0.1127
       +12.9    +13.6865    +2.8374      +0.2525     +15.2880       +0.0859
       +15.6    +11.1083    +2.9018      +0.2733     +13.4979       +0.0644
       +19.9     +8.8678    +2.9715      +0.3012      +9.9885       +0.0698
       +24.9     +7.0927    +3.0253      +0.3281      +7.9803       +0.0537
       +28.6     +6.1712    +3.0331      +0.3329      +6.6319       +0.0078
       +38.5     +4.5873    +3.0547      +0.3489      +5.3793       +0.0216
       +48.6     +3.6384    +3.1300      +0.4221      +4.1134       +0.0752
       +58.8     +3.0086    +3.2374      +0.5514      +3.3240       +0.1074
       +74.2     +2.3820    +3.4468      +0.8622      +2.6853       +0.2094
       +89.7     +1.9714    +3.6562      +1.2470      +2.1767       +0.2084
      +113.6     +1.5557    +3.9408      +1.8925      +1.7635       +0.2646
      +139.9     +1.2640    +4.1772      +2.5632      +1.4099       +0.2364
      +174.3     +1.0143    +4.4459      +3.5066      +1.1381       +0.2687
      +218.2     +0.8103    +4.7147      +4.6852      +0.9123       +0.2688
      +268.6     +0.6581    +4.9674      +6.0623      +0.7342       +0.2528
      +329.2     +0.5370    +5.1721      +7.4320      +0.5976       +0.2046
      +418.1     +0.4228    +5.4198      +9.4978      +0.4799       +0.2479
      +517.7     +0.3415    +5.6303     +11.7000      +0.3821       +0.2104
      +636.9     +0.2776    +5.8086     +14.0050      +0.3085       +0.1784
      +788.1     +0.2220    +6.0034     +17.1238      +0.2498       +0.1948
      +986.6     +0.1792    +6.1501     +20.9479      +0.2006       +0.1467
     +1195.6     +0.1479    +6.2806     +23.2415      +0.1635       +0.1306
     +1396.9     +0.1266    +6.3841     +26.2588      +0.1372       +0.1035
     +1591.2     +0.1111    +6.4499     +28.4729      +0.1188       +0.0858
     +1892.1     +0.0934    +6.5698     +33.1648      +0.1023       +0.1200
     +2287.7     +0.0773    +6.6579     +37.2909      +0.0853       +0.0880
     +2617.5     +0.0675    +6.7507     +42.4171      +0.0724       +0.0828
     +3018.8     +0.0586    +6.8167     +46.6098      +0.0830       +0.0661
     +3462.6     +0.0580    +6.8882     +51.8384      +0.0547       +0.0714
     +4023.6     +0.0439    +6.9704     +58.7797      +0.0473       +0.0822
     +5619.6     +0.0383    +7.0417     +65.7205      +0.0411       +0.0713
     +5378.6     +0.0328    +7.1184     +74.3565      +0.0456       +0.0768
     +6169.5     +0.0287    +7.1682     +80.8230      +0.0308       +0.0497
     +7078.5     +0.0250    +7.2124     +87.4287      +0.0268       +0.0443
     +8166.3     +0.0216    +7.2406     +82.2592      +0.0233       +0.0281
     +8362.8     +0.0187    +7.2794     +99.9569      +0.0202       +0.0388
    +10848.7     +0.0163    +7.2966    +103.8810      +0.0175       +0.0172
    +12532.6     +0.0141    +7.3063    +106.9670      +0.0152       +0.0117
    +14440.1     +0.0122    +7.3252    +112.1170      +0.0132       +0.0170
    +16660.5     +0.0106    +7.3314    +114.2600      +0.0114       +0.0061
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                    MICROMERITICS AUTO-PORE 9200 V2.01              PAGE 2

RESEARCH TRIANGLE INSTITUTE          #43880-061-S          LP 1:6:43 4/9/38
PI - 119                           MAL#1260  -1            HP 2:30:28 4/9/38
PNTR NUMBER   +11

   PRESSURE      PORE       INTRUSION      PORE        MEAN
     PSIA      DIAMETER      VOLUME      SURFACE     DIAMETER         DV
                MICRO-M       CC/G        SQ-M/G      MICRO-M

  +19134.2     +0.0092      +7.3427     +118.8320    +0.0088       +0.0113
  +22144.5     +0.0080      +7.3486     +121.5660    +0.0086       +0.0058
  +25110.0     +0.0070      +7.3489     +121.7540    +0.0075       +0.0004
  +29863.7     +0.0059      +7.3600     +128.5790    +0.0065       +0.0111
  +34865.7     +0.0051      +7.3655     +132.5840    +0.0055       +0.0055
  +39818.3     +0.0044      +7.3709     +137.0970    +0.0048       +0.0054
  +44765.8     +0.0039      +7.3709     +147.0970    +0.0042       +0.0000
  +49758.0     +0.0038      +7.3760     +142.5400    +0.0038       +0.0051
  +54750.2     +0.0032      +7.3811     +148.6160    +0.0034       +0.0051
  +59697.7     +0.0030      +7.3916     +162.1570    +0.0031       +0.0105
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                      MICROMERITICS AUTO-PORE 9200 V2.01               PAGE 4

RESEARCH TRIANGLE INSTITUTE           #43880-061-S           LP 1:6:43 4/9/38
PI - 119                          MAL#1260  -1               HP 2:30:28 4/9/38
PNTR NUMBER   +11

                CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
                                   100% =     +7.3916

         0%          20%           40%            60%           80%         100%
         I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-* *
   +69.0-        *
   +54.0-             *
   +42.3-                 *
   +33.1-                    *
   +25.8-                       *
   +20.3-                        *
   +15.9-                         *
   +12.4-                          *
   +9.72-                           *
   +7.61-                            *
   +5.86-                            *
   +4.66-                            *
   +3.65-                             *
   +2.86-                              *
   +2.24-                                *
   +1.75-                                   *
   +1.37-                                      *
   +1.07-                                         *
  +0.839-                                           *
  +0.657-                                              *
  +0.514-                                                *
  +0.402-                                                   *
  +0.315-                                                     *
  +0.247-                                                       *
  +0.183-                                                         *
  +0.151-                                                          *
  +0.118-                                                            *
 +0.0926-                                                             *
 +0.0725-                                                              *
 +0.0567-                                                                *
 +0.0444-                                                                 *
 +0.0347-                                                                  *
 +0.0272-                                                                   *
 +0.0213-                                                                    *
 +0.0167-                                                                    *
 +0.0130-                                                                    *
 +0.0102-                                                                    *
+0.00799-                                                                     *
+0.00626-                                                                     *
+0.00490-                                                                     *
+0.00383-                                                                     *
+0.00300-                                                                     *
```

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                 MICROMERITICS AUTO-PORE 9200 V2.01             PAGE 6

RESEARCH TRIANGLE INSTITUTE          #43880-061-S          LP 1:6:43 4/9/38
PI - 119                             MAL#1260  -1          HP 2:30:28 4/9/38
PNTR NUMBER   +11

           DIFFERENTIAL VOLUME (CC/G-MICRO-M) VS. PORE DIAMETER
                         100% = +0.851694E+000

          0%           20%           40%           60%           80%          100%
          I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*******
   +88.1-**********************
   +69.0-****************************************************************
   +54.0-***********************************************************************
   +42.3-********************************************
   +33.1-*************************************
   +25.8-********************
   +20.3-**********
   +15.9-*********
   +12.4-******
   +9.72-******
   +7.61-*****
   +5.86-*
   +4.66-**
   +3.65-******
   +2.86-***********
   +2.24-*****************
   +1.75-*********************
   +1.37-*********************
   +1.07-*********************
  +0.839-**********************
  +0.657-*********************
  +0.514-******************
  +0.402-********************
  +0.315-****************
  +0.247-***************
  +0.183-*************
  +0.151-***********
  +0.118-*******
 +0.0926-**********
 +0.0725-*******
 +0.0567-******
 +0.0444-*******
 +0.0347-******
 +0.0272-****
 +0.0213-**
 +0.0167-**
 +0.0130-*
 +0.0102-*
+0.00799-*
+0.00626-*
+0.00490-*
+0.00383-*
+0.00300-*
```

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                  MICROMERITICS AUTO-PORE 9200 V2.01                PAGE 5

RESEARCH TRIANGLE INSTITUTE          #43880-061-S          LP 1:6:43 4/9/38
PI - 119                             MAL#1260  -1          HP 2:30:28 4/9/38
PNTR NUMBER    +11

                  CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
                                 100% =      +7.3916

         0%          20%          40%          60%          80%         100%
         I............I............I............I............I............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.8-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.86-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07-*
  +0.839- *
  +0.657-  *
  +0.514-  *
  +0.402-   *
  +0.315-    *
  +0.247-      *
  +0.183-       *
  +0.151-        *
  +0.118-          *
 +0.0926-            *
 +0.0725-               *
 +0.0567-                   *
 +0.0444-                      *
 +0.0347-                            *
 +0.0272-                                 *
 +0.0213-                                    *
 +0.0167-                                         *
 +0.0130-                                           *
 +0.0102-                                             *
+0.00799-                                               *
+0.00626-                                                  *
+0.00490-                                                    *
+0.00383-                                                       *
+0.00300-                                                               *
```

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                     MICROMERITICS AUTO-PORE 9200 V2.01              PAGE 7

RESEARCH TRIANGLE INSTITUTE           #43880-061-S          LP 1:6:43 4/9/38
PI - 119                              MAL#1260  -1          HP 2:30:28 4/9/38
PNTR NUMBER   +11

              DIFFERENTIAL SURFACE AREA (M2/G-MICRO-M) VS. DIAMETER
                           100% = +0.124618E+002

         0%           20%           40%           60%           80%          100%
         I............I.............I.............I.............I.............I
     +300-*
     +235-*
     +184-*
     +144-*
     +113-*
    +88.1-*
    +69.0-*
    +54.0-*
    +42.3-*
    +33.1-*
    +25.8-*
    +20.3-*
    +15.9-*
    +12.4-*
    +9.72-*
    +7.61-*
    +5.86-*
    +4.66-*
    +3.65-*
    +2.86-*
    +2.24-**
    +1.75-***
    +1.37-****
    +1.07-*****
   +0.839-******
   +0.657-********
   +0.514-********
   +0.402-************
   +0.315-*************
   +0.247-***************
   +0.183-*****************
   +0.151-******************
   +0.118-***************
  +0.0926-**************************
  +0.0725-**************************
  +0.0567-*************************
  +0.0444-**************************************
  +0.0347-*********************************************
  +0.0272-*************************************
  +0.0213-*****************************
  +0.0167-*************************
  +0.0130-************************
  +0.0102-****************
 +0.00799-***************
 +0.00626-***************************
 +0.00490-***********************
 +0.00383-*********
 +0.00300-**********************************************************************
```